FLUIDITY AND PLASTICITY

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BY

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To my sister

Anna

PREFACE

Our knowledge of the flow of electrical energy long ago developed into the science of Electricity but our knowledge of the flow of *matter* has even yet not developed into a coordinate science. In this respect the outcome of the labors of the hydrodynamicians has been disappointing. The names of Newton, Navier, Poisson, Graham, Maxwell, Stokes and Helmholtz with a thousand others testify that this field has been well and competently tilled. Even from the first the flow of liquids has been a subject of practical importance, yet the subject of Hydraulics has never become more than an empirical subject of interest merely to the engineer.

Unfortunately the theory is complicated in that the flow of matter may be hydraulic (turbulent), viscous (linear), or plastic, dependent upon the conditions. It was in 1842 that viscous flow was first differentiated from hydraulic flow, and only now are we coming to realize the important distinction between viscous and plastic deformation. Considering the confusion which has existed in regard to the character of flow, it is not surprising that there has been uncertainty in regard to precise methods of measurement and that exact methods have been discovered, only to be forgotten, and rediscovered independently later. As a result, the amount of really trustworthy data in the literature on the flow of matter under reproducible conditions is limited, often to an embarrassing extent.

If we are to have a theory of flow in general, we must consider matter in its three states. No such general theory has appeared, although one is manifestly needed to give the breath of life to the dead facts about flow. The author offers the theory given in the following pages with the utmost trepidation. Although he has given several years to the pleasant task of supporting its most important conclusions, a lifetime would be far too short to complete the work unaided. The author makes no apology for any lack of finality. Parts of the theory which have already

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found their way into print have awakened a vigorous discussion which is still in progress. This is well, for our science thrives on criticism and through the collaboration of many minds the final theory of flow will be evolved.

Without going considerably beyond the limits which we have placed upon ourselves, it is impossible to refer even briefly to all of the important papers on the subject. References given in the order that they come up in the discussion are not the best suited for later reference. The novel plan has been tried of placing nearly all of our references in a separate appendix which is also an author index and is, therefore, arranged alphabetically under the authors' names. In the text the name of the author and the year of publication of the monograph is usually sufficient for our purpose, but sometimes the page is also added. The titles of the monographs are usually given in the hope that this bibliography may be of considerable service to investigators who are looking up a particular line of work connected with this general subject.

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EUGENE C. BINGHAM.

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PART I

VISCOMETRY

CHAPTER I

PRELIMINARY. METHODS OF MEASUREMENT

Introductory.—What one may be pleased to call "dominant ideas" have so stimulated the work on viscosity, that it would be entirely possible to treat the subject of viscosity by considering in turn these dominant ideas.

Practically no measurements from which viscosities may be calculated were made prior to 1842, yet very important work was being done in Hydrodynamics, and the fundamental laws of motion were established during this preliminary period. To this group of investigations belong the classical researches of Bernouilli (1726), Euler (1756), Prony (1804), Navier (1823), and Poisson (1831). In the development of Hydrodynamics much experimental work was done upon the flow of water in pipes of large bore by Couplet (1732), Bossut (1775), Dubuat (1786), Gerstner (1800), Girard (1813), Darcy (1858), but this work could not lead to the elucidation of the theory of viscosity as we shall see. Important work belonging to this preliminary period was also done by Mariotte (1700), Galileo (1817), S'Gravesande (1719), Newton (1729), D'Alembert (1770), Boscovich (1785), Coulomb (1801), Eytelwein, (1814).

It is to Poiseuille (1842) that we owe our knowledge of the simple nature of flow in capillary spaces, which is in contrast with the complex condition of flow in wide tubes, heretofore used. He wished to understand the nature of the flow of the blood in the capillaries, being interested in internal friction from the physiological point of view. He made a great many meas-

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urements of the rates of flow of liquids through capillary tubes, which are still perhaps unsurpassed. They lead directly to the laws of viscous resistance and they will be described in detail in a later chapter. The theoretical basis for these laws and a definition of viscosity were supplied by the labors of Hagen (1854), G. Wiedemann (1856), Hagenbach (1860), Helmholtz (1860), Maxwell (1860). Since the velocity of flow through the capillary may be considerable, a correction is generally necessary for this kinetic energy, which is transformed into heat. Hagenbach was the first to attempt to make this correction but Neumann (1858) and Jacobson (1860) were the first to put the correction into satisfactory form. Thus both the method of measurement and the formula used in calculation of absolute viscosities were practically the same by 1860 that they are today. Unfortunately, these important researches have not been sufficiently well-known, hence their results have been repeatedly rediscovered, and there is an evident confusion in the minds of many as to the conditions necessary for exact measurement. The so-called "transpiration" or Poiseuille method was not the only one which was worked out during this period of perfecting the methods of measurement. The pendulum method was developed by Moritz (1847), Stokes (1849), O. E. Meyer (1860), Helmholtz (1860) and Maxwell (1860). The well-known method of the falling sphere was worked out by Stokes (1849).

During the period to which we have just referred, Graham (1846–1862) had been doing his important work on gases, but the development of the kinetic theory gave a great impetus to the study of the viscosity of gases; and at the hands of Maxwell, O. E. Meyer and others, viscosity in turn gave the most striking confirmation to the kinetic theory. The work on the viscosity of gases has continued on until the present, being done almost exclusively by physicists.

To chemists, on the other hand, impressed by the relations between physical properties and chemical composition, so forcibly brought to their attention by the work of Kopp, the viscosity of liquids has been an interesting subject of study. To this group belong the researches of Graham (1861), Rellstab (1868), Guerout (1875), Pribram and Handl (1878), Gartenmeister (1890), Thorpe and Rodger (1893) and many others.

The rise of modern physical chemistry resulted in an awakening of interest in all of the properties of aqueous solutions. Along with other properties, viscosity received attention from a great number of physical chemists, among whom we may cite Arrhenius (1887), Wm. Ostwald (1893), J. Wagner (1883–90), Reyher (1888), Mützel (1891). It must be admitted that our knowledge of viscosity has not played an important part in the development of modern physical chemistry. It is doubtless for this reason that the subject of viscosity is left unconsidered in most textbooks of physical chemistry. It is certainly not because viscosity does not play an important role in solutions, but rather that the variables in the problem have not been properly estimated. That with the physical chemist viscosity has so long remained in the background, makes it all the more promising as a subject of study, particularly since it is becoming more and more nearly certain that viscosity is intimately related to many very diverse properties such as diffusion, migration of ions, conductivity, volume, vapor-pressure, rate of solution and of crystallization, as well as chemical composition and constitution, including association and hydration. It seems probable that the work in this field is going to expand rapidly, for it is becoming imperative that the exact relation between viscosity and conductivity, for example, should be clearly demonstrated.

With the recent advances in our knowledge of the nature of colloids, there was certain to be an extended study of the viscosity of these substances, because no property of colloids is so significant as the viscosity. This in turn has again stimulated interest in viscosity on the part of the physiologist, so that the viscosity of blood, milk, and other body fluids have been repeatedly investigated under the most varied conditions during the past few years.

The use of viscosity measurements for testing oils, paints, and various substances of technical interest has given rise to a series of investigations, that of Engler (1885) being among the earliest and most important in this group. These researches have been devoted largely to devising of instruments and to a comparison of the results obtained.

Quite unrelated to the above groups for the most part, are the investigations which have undertaken to study the viscosity

of solids.   The study of elasticity has been the dominant idea
in this group of researches.

Very little work has been done upon the viscosity of matter
in the different states of aggregation taken as a whole.   If it
has been shown that our knowledge of viscosity consists of
somewhat unrelated groups, it is equally apparent that such a
separation is artificial and that nothing could be more important
for our complete understanding of viscosity, than to bring these
groups together into an inter-related whole.   We shall therefore
not make an attempt to follow the chronological method, where
it interferes with the consideration of the subject as a whole.
Nevertheless the groups of researches to which we have alluded
stand out rather clearly.   The methods of measurement in use
will be first considered, after which we shall study the viscosities
of liquids, solutions, solids, and gases respectively.

Elastic Deformation, Plastic, Viscous, and Turbulent Flow.—
If a perfectly elastic solid be subjected to a shearing stress a
certain strain is developed which *entirely* disappears when the
stress is removed.   The total work done is zero, the process is
reversible, and viscosity can play no part in the movement.
This is not a case of flow but of elastic deformation.   If a body
which is imperfectly elastic as regards its form be subjected to
shearing stress, it will be found that a part, at least, of the
deformation will remain long after the stress is removed.   In this
case work has been done in overcoming some kind of internal
friction.   We may distinguish the kinds of flow under *three
régimes*.   It is characteristic of *viscous or linear flow* that the
amount of deformation is directly proportional to the deforming
force, and the ratio of the latter to the former gives a measure
of viscosity.   It has been questioned at times whether this ratio
is truly constant, but it appears that only one qualification is
necessary.   In very viscous substances time may be necessary
for the flow to reach a steady state, aside from any period of
acceleration, because with substances like pitch the viscous
resistance develops slowly, so that the above ratio gradually
increases when the load is first put on, but even in this case the
ratio finally reaches a value which is independent of the amount
of the load.   As, however, the deforming force is steadily in-
creased, a point may be reached where the above ratio suddenly

decreases. At this point the régime of *turbulent* or *hydraulic flow* begins. This will be studied in detail at a later point in the development of the subject. There are substances, on the other hand, for which the value of the above ratio increases indefinitely as soon as the deforming force falls below a certain minimum. These substances are said to be plastic. In *plastic flow* it is generally understood that a definite shearing force is required before any deformation takes place. But whether this is *strictly* true or not has not been established.

The Coefficient of Viscosity.—Consider two parallel planes A and B, s being their distance apart. If a shearing force F per unit area give the plane A a velocity v in reference to B, the velocity of each stratum, between A and B, as was first pointed out by Newton, will be proportional to its distance from B. The rate of shear dv/ds is therefore constant throughout a homogeneous fluid under the above conditions. The possibility that it may not be constant near a boundary surface will be considered later. Since the force F is required to maintain a uniform velocity, this force must be opposed by another which is equal in amount due to the internal friction. The ratio of this force to the rate of shear is called the coefficient of viscosity and is usually denoted by the symbol η

$$\eta = \frac{Fs}{v} \tag{1}$$

The dimensions of viscosity are $[ML^{-1}T^{-1}]$. The definition of viscosity due to Maxwell may be stated as follows: The viscosity of a substance is measured by the tangential force on a unit area of either of two horizontal planes at a unit distance apart required to move one plane with unit velocity in reference to the other plane, the space between being filled with the viscous substance. The *coefficient of fluidity* is the reciprocal of the coefficient of viscosity, so that if the former is denoted by ϕ we have $\phi = \dfrac{1}{\eta}$. The coefficient of fluidity may be independently defined as the velocity given to either of two horizontal planes in respect to the other by a unit tangential force per unit area, when the planes are a unit distance apart and the space between them is filled with the viscous substance.

Methods of Measurement.—Almost numberless instruments have been devised for the measurement of viscosity, but the greater part of these are suitable for giving relative values only. There are, however, several quite distinct methods which are susceptible of mathematical treatment so that *absolute viscosities* may be obtained. The possible methods for measuring viscosity may be classified under three heads as follows:

1. The measurement of the resistance offered to a moving body (usually a solid) in contact with the viscous fluid.

2. The measurement of the rate of flow of a viscous fluid.

3. Methods in which neither the flow nor the resistance to flow are measured.

1. The various methods for measuring viscosity while maintaining the fluid in a nearly fixed position, together with the names of investigators who have developed the method are as follows:

(*a*) A horizontal disk supported at its middle point by a wire and oscillating around the wire as an axis. Coulomb (1801), Moritz (1847), Stokes (1850), Meyer (1865), Maxwell (1866), Grotrian (1876), Oberbeck (1880), Th. Schmidt (1882), Stables and Wilson (1883), Fawsitt (1908).

(*b*) A sphere filled with liquid and oscillating around its vertical axis. Helmholtz and Piotrowski (1868), Ladenburg (1908).

(*c*) A cylinder filled with liquid and oscillating around its vertical axis. Mützel (1891).

(*d*) Concentric cylinders. The outside one is rotated at constant velocity and the torque, exerted upon the inner coaxial cylinder which is immersed in the viscous fluid, is measured. Stokes (1845), de St. Venant (1847), Boussinesq (1877), Couette (1888), Mallock (1888), Perry (1893).

(*e*) An oscillating solid sphere immersed in the viscous substance and supported by bifilar suspension was used by König (1885).

(*f*) A body moving freely under the action of gravity, *e.g.*, falling sphere of platinum, mercury, or water, a falling body of other shape than a sphere, a rising bubble of air. Stokes (1845), Pisati (1877), Schöttner (1879), de Heen (1889), O. Jones (1894), Duff (1896), J. Thomson (1898), Tammann (1898), Schaum (1899), Allen (1900), Ladenburg (1906), Valenta (1906), Arndt (1907).

2. The methods for measuring the rate of flow of a viscous fluid:

(*a*) Efflux through horizontal tubes of small diameter. Gerstner (1798), Girard (1816), Poiseuille (1842), G. Wiedemann (1856), Rellstab (1868), Sprung (1876), Rosencranz (1877), Grotrian (1877), Pribram and Handl (1878), Slotte (1881), Stephan (1882), Foussereau (1885), Couette (1890), Brückner (1891), Thorpe and Rodger (1893), Hosking (1900), Bingham and White (1912).

(*b*) Efflux through a vertical tube of small diameter. Stephan (1882),

Engler (1885), Arrhenius (1887), Ostwald (1893), Gartenmeister (1890), Heydweiller (1895), Friedländer (1901), McIntosh and Steele (1906), Rankine (1910).

(c) Efflux through a bent capillary. Grüneisen (1905).

(d) Bending of beams and torsion of rods of viscous substance. Trouton (1906), Trouton and Andrews (1904).

(e) Rate at which one substance penetrates another under the influence of capillary action, diffusion, or solution tension.

3. Other methods for measuring viscosity:

(a) Decay of oscillations of a liquid in U-shaped tubes. Lambert (1784).

(b) Decay of waves upon a free surface. Stokes (1851), Watson (1902).

(c) Decay of vibrations in a viscous substance. Guye and Mintz (1908).

(d) Rate of crystallization. Wilson (1900).

Nomenclature.—A great variety of names have been given to instruments devised for measuring viscosity, among which we may cite viscometer, viscosimeter, glischrometer, microrheometer, stalagnometer, and viscostagnometer. All but the first two are but little used and their introduction seems an unnecessary complication. Viscometer and viscosimeter are about equally used in England and America, but such a standard work as Watt's Dictionary uses only viscometer. Viscosimeter in its German equivalent *Viskosimeter* is entirely satisfactory, but in English viscosímeter is apt to be mispronounced viscósimeter. Furthermore viscosimeter does not so easily relate itself in one's mind to viscometry which is the only word recognized in the standard dictionaries to denote the measurement of viscosity. Professor Brander Matthews kindly informs me that the formation of the word viscometer is quite as free from objection as that of viscosimeter, and viscometer is in harmony with modern spelling reform. Hence viscometer should be adopted as the name for all instruments used for measuring viscosity. The different forms are distinguished by the names of their inventors.

THE LAW OF POISEUILLE

Experimental Verification.—Prior to 1842 it had not been established as a fact that the movement of the blood through the capillaries has its origin solely in the contractions of the heart. There were theories current that the capillaries themselves caused the flow of blood or that the corpuscles were instrumental in producing it. Poiseuille reasoned that if the lengths and diameters of the capillaries are different in the various warm-blooded animals and if the pressure and temperature of the blood vary in different parts of the body, light might be thrown upon the problem by investigating the effects upon the rate of flow in capillary tubes of changes in (1) pressure, (2) length of capillary, (3) diameter of capillary, and (4) temperature.

The results of Poiseuille's experiments were of a more fundamental character than he anticipated for they proved that the conditions of capillary flow are much simpler than those in the wide tubes which had previously been employed, and by his experiments the laws of viscous flow became established. Not only did Poiseuille perform experiments which resulted in the law which bears his name, and therefore have affected all subsequent work, but he measured the efflux times of water by the absolute method taking elaborate precautions to insure accuracy, and using capillaries of various lengths and diameters which are equivalent to separate instruments—in all over *forty* in number. Thus one is justified in studying his work in considerable detail, not only for its historic interest, but on account of its bearing upon questions which will arise later. In the Appendix his measurements are reproduced in full.

In Fig. 1 is shown the most essential part of the apparatus of Poiseuille. It consists of a horizontal glass capillary *d* joined to the bulb, whose volume between the marks *c* and *e* was accurately determined. The bulb is connected above with a tube which leads to (1) a 60-l reservoir for keeping the pressure of the air within the apparatus constant, (2) a manometer, filled with

water or mercury, and (3) a pump which is used for giving the desired pressure. The capillary opens into the distilled water of the bath in which the bulb and capillary are immersed. After the dimensions of the bulb and capillary have been found, it is only necessary, in making a viscosity determination at any given temperature, to observe the time necessary for a volume of liquid equal to that contained in the bulb to flow through the capillary under a determined pressure. Without going into detail at this point, it need be merely stated here that due means were taken for getting the true dimensions of the capillary and bulb, for filling the apparatus with clean pure liquid, and for estimating the mean effective pressure, which consists of the pressure obtained from the manometer plus the hydrostatic pressure from the bottom of the falling meniscus in the
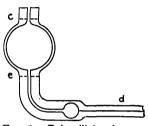
Fig. 1.—Poiseuille's viscometer.

bulb to the level of the capillary, minus the hydrostatic pressure from the level of the capillary to the surface of the bath, minus a correction for the capillary action in the bulb, and two corrections for the pressure of the atmosphere, which may be either positive or negative. One of these last corrections is due to the air within the apparatus being more dense than that outside, the other is due to the difference of pressure of the atmosphere upon the liquid surfaces in the upper arm of the manometer and in the bath, unless they happen to be at the same level.

Law of Pressures.—In obtaining this law all of the experiments were made at a temperature of 10°C. For a capillary of given length and diameter, the time of transpiration was measured for various pressures. For example, one capillary was 75.8 mm long, the major and minor axes of the end of the capillary nearer the bulb were 0.1405 and 0.1430 mm and those of the open end 0.1400 and 0.1420 mm respectively. The pressures used are given in the first column of Table I and the times of transpiration in column 2. One of these values is then employed to calculate the others on the assumption that *the times of transpiration are inversely proportional to the pressures*, as given in column 3.

TABLE I.—CAPILLARY A′

Pressure in millimeters of mercury at 10°C	Observed time for transpiration of 13.34085 cc of water	Calculated time	Per cent difference
97.764	10,361.0		
147.832	6,851.0	6,851.91	0.01
193.632	5,233.0	5,231.22	0.03
387.675	2,612.5	2,612.84	0.01
738.715	1,372.5	1,371.20	0.09
774.676	1,308.0	1,307.55	0.04

In the above case it is certainly true that the rate of flow is proportional to the pressure, but it is equally certain that this relation no longer holds when the capillary becomes sufficiently shortened. Thus when the length of the tube used above is shortened to 15.75 mm, the values given in Table II are obtained.

TABLE II.—CAPILLARY A′ⁱᵛ

Pressure in millimeters of mercury at 10°C	Observed time for transpiration of 13.34085 cc of water	Calculated time	Per cent difference
24.661	8,646		
49.591	4,355	4,299	−1.29
98.233	2,194	2,170	−1.09
148.233	1,455	1,438	−1.17
194.257	1,116	1,097	−1.63
388.000	571	549	−3.85
775.160	298	275	−7.72

Not only is there a marked deviation from the assumed law of pressures as soon as the capillary is sufficiently shortened, but the percentage difference between the observed and calculated values increases quite regularly as the pressure increases. But in either case, whether the capillary is shortened or the pressure increased, we note that the *velocity* is decreased. Whether the irregularity here observed is due to the use of some of the available work in imparting kinetic energy to the liquid, or it is due

to eddy currents which appear under conditions of hydraulic flow, we will reserve for later discussion. This question was not considered by Poiseuille, yet with a great variety of tables showing an agreement like that in Table I above, Poiseuille was fully justified in concluding that for tubes of very small diameters and of sufficient length, *the quantity of liquid which transpires in a given time and at a given temperature is directly proportional to the pressure*, or $V = Kp$, where K is a constant, V the volume, and p the pressure head, causing the flow through the tube.

Law of Lengths.—Poiseuille next studied the effect of the length of the tube upon the rate of flow, but this problem presented exceptional difficulty owing to the fact that tubes are never of uniform cross-section. With the *camera lucida* he examined and measured each section of the tubes, which had been carefully selected from a large number, and finally corrections were made for the small changes in diameter, assuming the law of diameters to be given later. This seems justified since the corrections were very small. In Table III the results are given which Poiseuille obtained with capillary "B." The lengths of the capillary are given in column 1, the major and minor axes of the free end in column 2, the time required for the transpiration

TABLE III.—CAPILLARY B

Length of tube in millimeters	Major and minor axes of free end	Time of transpiration of 6.4482 cc	Time calculated	Per cent. difference
100.050	$\left\{\begin{array}{l} 0.1135 \\ 0.1117 \end{array}\right\}$	2,052.98		
75.050	$\left\{\begin{array}{l} 0.1140 \\ 0.1120 \end{array}\right\}$	1,526.20	1,539.0	0.85
49.375	$\left\{\begin{array}{l} 0.1142 \\ 0.1122 \end{array}\right\}$	998.74	1,004.0	0.53
23.575	$\left\{\begin{array}{l} 0.1145 \\ 0.1123 \end{array}\right\}$	475.18	476.8	0.34
9.000	$\left\{\begin{array}{l} 0.1144 \\ 0.1124 \end{array}\right\}$	199.39	181.4	−9.05
3.900	$\left\{\begin{array}{l} 0.1145 \\ 0.1125 \end{array}\right\}$	110.20	86.4	−21.64

of the 6.4482 cc of water at 10°C contained in the bulb at a constant pressure of 775 mm of mercury are given in column 3. Assuming that the time of flow is directly proportional to the length of the tube, Poiseuille used the time of one experiment to calculate the one immediately succeeding, and thus are obtained the values given in column 4. It is evident that the last two lengths are too short, but the others fairly substantiate the law. The agreement is still better when corrections are made for the varying diameters of the tube. This correction is especially important since, as will be shown, the efflux rate varies as the fourth power of the diameter. From results like those exhibited in Table III Poiseuille concluded that *the quantity of liquid passing through a tube of very small diameter at a given temperature and pressure varies inversely as the length,* and we have that $V = K''p/l$ where l represents the length. But the last two observations show that this law has its limitations.

Law of Diameters.—To discover the relation between the diameter of the capillary and the rate of flow, Poiseuille calculated the quantity of water which would flow through 25 mm of the different tubes at 10°C under a pressure of 775 mm of mercury in 500 seconds, obtaining the values given in Table IV.

TABLE IV

Designation of tube	Mean diameter of tube in centimeters	Volume efflux in 500 sec. from observations	Volume calculated	Per cent. difference
M	0.0013949	0.0014648	0.001465	+0.02
E	0.0029380	0.0288260	0.028808	−0.07
D	0.0043738	0.1415002	0.141630	+0.10
C	0.0085492	2.0673912	2.066930	−0.02
B	0.0113400	6.3982933	6.389240	−0.14
A	0.0141600	15.5328451	15.547100	+0.10
F	0.0652170	6,995.8702463		

The volumes calculated in the fourth column are obtained by comparing each tube with the one following on the assumption that *the quantity traversing the tube is proportional to the fourth power of the diameter,* thus $\overline{0.002938}^4 : \overline{0.0013949}^4 = 0.028826 : x$, or $x = 0.001465$. The agreement is very satisfactory, hence the

formula becomes $V = K \dfrac{pd^4}{l}$. For water at 10°C he found the
value of K to be quite exactly 2,495,224, p being expressed in
millimeters of mercury at 10° and l and d in centimeters. He
experimented with alcohol and mixtures of alcohol and water
and for these we obtain different values of K. Poiseuille did
not use the terms viscosity or fluidity, nevertheless these values
of K are proportional to the fluidity.

The Effect of Temperature on the Rate of Flow.—Girard had
given a formula to represent the flow of water in a pipe as a
function of the temperature, but the constants had to be deter-
mined for each pipe. Poiseuille gave a formula which was inde-
pendent of the instrument used,

$$Q = 1{,}836{,}724{,}000 \left(1 + 0.0336793T + 0.0002209936T^2\right)\frac{pd^4}{l}$$

where Q represents the *weight* of water traversing the capillary
in a unit of time. The adequacy of this formula to reproduce
the observed values is shown in Table V.

TABLE V.—CAPILLARY A

$l = 10.05$ cm $d = 0.0141125$ cm $p = 776$ mm of mercury. Time of
flow 1,000 sec.

TEMPERATURE	WEIGHT OF EFFLUX OBSERVED	WEIGHT OF EFFLUX CALCULATED BY FORMULA
0.6	5.74376	5.73955
5.0	6.60962	6.60381
10.0	7.64649	7.64435
15.0	8.74996	8.74705
20.0	9.91530	9.91191
25.0	11.14584	11.13892
30.1	12.45631	12.45423
35.1	13.80695	13.80710
40.1	15.21866	15.22184
45.0	16.67396	16.66860

Since the values calculated are weights and not volumes, the
values of Q are not proportional to the fluidity. This formula
remains empirical, but the expression $V = K \dfrac{pd^4}{l}$ can be readily
derived from the fundamental laws of motion.

Theoretical Derivation of the Law.—Hagenbach (1860) appears
to have been the first to give a definition of viscosity. He made

a very careful study of the earlier work on viscosity and gave a theoretical derivation of the law of Poiseuille, which has had very great effect upon the succeeding history of this subject. Neumann gave the deduction of the Law of Poiseuille in his lectures on Hydrodynamics in 1858, and thus prior to the publication of Hagenbach's paper in March, 1860. This deduction was first published by Jacobson early in 1860 and the lectures were published in full in 1883. In April, 1860 Helmholtz published the derivation of the law from the equations of motion. J. Stephan (1862) and Mathieu (1863) gave independent derivations of the law. Reference should also be made to the treatment of the flow in long narrow tubes by Stokes (1849).

Imagine a horizontal capillary whose bore is a true cylinder to connect two reservoirs L (left) and R (right) there being a difference of pressure between the two reservoirs, at the level of the capillary, amounting to p grams per square centimeter. If the pressure in L is the greater the direction of flow through the capillary will be from left to right. The total effective pressure p is used up in doing various forms of work, several of which can be differentiated with a resultant gain in clearness of understanding of the conditions of flow.

. 1. Near the entrance to the capillary the particles of fluid undergo a rapid acceleration; this absorption of kinetic energy causes a fall in the pressure amounting to p_k.

2. Within the capillary, there may be a finite movement of the fluid over the walls of the tube, due to *slipping*. Unless the external friction is zero or infinity, work will be done and there will be a fall of pressure p_s.

3. Unless the external friction is zero, the layers of fluid nearer the walls of the tube will move more slowly than the layers nearer the axis of the tube, and an absorption of pressure due to this internal friction will result. Let this be p_v.

4. If the path of the particles through the capillary is not perfectly linear, the additional distance travelled in the *eddies*, will give rise to a further drop in the pressure amounting to p_e. This *turbulent flow* is certain to occur when the velocity of flow becomes sufficiently high.

5. But even before the velocity becomes turbulent it seems possible that the stream lines at the extremities of the tube may

be somewhat distorted, in which case there must be a drop in pressure p_s.

6. Heat is produced as the fluid passes through the tube and therefore the temperature may be different at different points of the tube and since the temperature greatly affects the viscosity of most substances, this may affect the amount of work done in the passage through the tube. If the fluid is incompressible it will have the same mean velocity through each cross-section of the capillary, and the pressure must fall in a linear manner at least so long as the flow is linear. If on the other hand the substance is compressible, the velocity must increase as the fluid passes through the tube, because of the expansion which results from the decrease of pressure. With the expansion there is a lowering of the temperature. Let the resultant effect of these changes in the temperature upon the effective pressure be p_T. It may be either positive or negative.

At the exit of the capillary the fluid has no effective pressure but it still possesses all of its kinetic energy which causes the fluid to go for a considerable distance out into the reservoir R, dragging some of the fluid in R with it and producing eddies, so that the kinetic energy is finally dissipated in overcoming viscous resistance outside of the capillary, and not in adding to the effective pressure, as Applebey (1910) has supposed.

The sum of these possible losses of effective pressure is then

$$p = p_k + p_s + p_v + p_e + p_s + p_T \qquad (2)$$

We shall consider first the case where $p = p_v$, supposing that the fluid is incompressible, as is nearly the case in liquids.

Let the radius of the capillary be R and the radius of a hollow cylinder coaxial with the capillary be r. It is evident from the symmetrical arrangement that at every point in such a cylinder, the velocity must be identical. Let this velocity be v. The rate of deformation must be $\dfrac{dv}{dr}$ and the tangential force due to the viscous resistance, acting from right to left, will be $\eta \dfrac{dv}{dr}$ (*cf.* Eq. (1)). Over the whole surface of the cylinder whose length is l, this force must amount to

$$2\pi r l . \eta \, \frac{dv}{dr}$$

But the force due to the frictional resistance on the outside of the cylinder must be exactly balanced by a force due to the pressure and this is

$$- \pi r^2 pg$$

where p is the pressure in grams per square centimeter and g is the acceleration due to gravity. The negative sign is used because this force acts from left to right. We have then that

$$dv = - \frac{pg}{2l\eta} rdr$$

$$v = - \frac{pgr^2}{4l\eta} + K$$

but $v = 0$ when $r = R$, therefore the constant of integration K can be evaluated

$$K = \frac{pgR^2}{4l\eta}$$

$$v = \frac{pg}{4l\eta} (R^2 - r^2) \tag{3}$$

From Eq. (3) we may obtain the velocity in centimeters per second at any point in the capillary. It follows that the liquid flowing through the capillary in a given time has the volume of a paraboloid of revolution. If the volume per second is U, then

$$U = -\pi \int_{r=0}^{r=R} r^2 dv = \frac{\pi pg}{2l\eta} \int_{r=0}^{r=R} r^3 dr = \frac{\pi gpR^4}{8l\eta} \tag{4}$$

which is the Law of Poiseuille. If V is the total volume of efflux in the time t, the formula becomes

$$V = \frac{\pi gpR^4 t}{8l\eta} \tag{5}$$

The mean velocity of the fluid, in cubic centimeters per second passing through the tube, I, is

$$I = \frac{V}{\pi R^2 t} = \frac{pgR^2}{8l\eta} \tag{6}$$

Summary.—The simple law of Poiseuille was first discovered experimentally, after which its theoretical deduction was quickly made. There is, however, a considerable amount of data for which the simple law is not sufficient. The law may be given far greater usefulness by adding certain correction terms, which are the subject of discussion in the following chapter.

THE AMPLIFICATION OF THE LAW OF POISEUILLE

The Kinetic Energy Correction.—In deriving the law in the preceding chapter, we limited ourselves to the simplest case, where all of the energy is employed in overcoming viscous resistance within the fluid, or $p = p_v$. It is desirable however that the law be given a wider application, and that the law be tested under the most varied conditions. In the experiments which Poiseuille used to verify his law, the kinetic energy correction was negligible, but the time necessary for a single determination was often excessive, consuming several hours. It is to be recalled at this point that in some of his experiments, in which the rate of flow was higher than in the others, the law was not verified. Poiseuille and others have been greatly troubled in their viscosity determinations by dust particles becoming lodged in the capillary. If it were possible therefore to employ higher speeds, not only would there be an economy in time but the dust particles would be much more likely to be swept out from the tube. However in using these higher velocities a correction for the loss in kinetic energy must be applied.

Hagenbach (1860) is the first one to attempt to make this correction, the results of whose work became generally known, although it appears that Neumann prior to 1860 had made the correction in nearly its present form. The work of Neumann was reported by Jacobson in 1860 but his work has also remained but little known to workers in this field. Gartenmeister (1890) reported that Finkener had arrived at a correction which differed from that of Hagenbach, but Finkener seems not to have published any monograph on the subject stating why he considered his correction superior. However Couette in the same year (1890) published a very important paper in which he arrived independently at the same correction as that given by Neumann and Finkener, and a year later Wilberforce (1891) independently attacked the same subject and showed that there is a slip in the

reasoning of Hagenbach. He showed that Hagenbach should
have reached a value which is identical with that given by the
others. The correction may be simply deduced as follows:

The kinetic energy of the fluid passing any cross-section of a
cylindrical tube per unit of time is

$$\int_0^R 2\pi r\, dr \rho v \cdot \frac{v^2}{2} = \frac{\pi \rho p^3 g^3}{64 l^3 \eta^3} \int_0^R (R^2 - r^2)^3 r\, dr = \pi \rho R^2 I^3$$

where ρ is the density of the fluid. Since the volume of fluid
passing any cross-section per unit of time is $\pi R^2 I$, the energy sup-
plied in producing the flow is $\pi R^2 I p g$, hence, the energy converted
into heat within the tube must be $\pi R^2 I (pg - \rho I^2)$. From Eqs. (2)
and (6) we have

$$p_k g = \rho I^2 = \frac{\rho V^2}{\pi^2 R^4 t^2} \tag{7}$$

Thus taking into account the loss in kinetic energy, the formula
of Poiseuille becomes

$$\eta = \frac{\pi g p R^4 l}{8 V l} - \frac{m \rho V}{8 \pi l t} \tag{8}$$

in which m is a constant which according to the above derivation
is equal to unity. The formula of Hagenbach differed only in
that the constant m is equal to $2^{-\frac{1}{3}}$ or 0.7938.

It is of historical interest in this connection to note that Ber-
nouilli's assumption that all of the particles flowing through a pipe
have the same velocity, leads one to the conclusion that the
kinetic energy of the fluid passing any cross-section per unit of
time is exactly one-half of that given above or $\dfrac{\pi R^2 I^3}{2}$, and the
value of m in that case would be only 0.50. This value was actu-
ally suggested by Reynolds (1883) when the openings of the tubes
were rounded or trumpet-shaped, but $m = 0.752$ when the ends
are cylindrical. It may be added that Hagenbach compared his
value of 0.7938 with the observed values obtained by various
hydraulicians working with wide tubes, Hagen 0.76, Weisbach
0.815, Zeuner 0.80885, Morin 0.82, and Bossut 0.807, and he
found that his value was near the mean. But account should
have been taken of the fact that their results apply to the tur-
bulent régime, but not necessarily to the régime of linear flow.

Boussinesq (1891) while admitting the correctness of the

method used by Couette—and as we have seen, also by Neumann, Finkener, and Wilberforce—as a first approximation, gives a more rigorous treatment of the subject on the basis of the kinetic theory by which he finds $m = 1.12$.

Knibbs (1895) in a valuable discussion of the viscosity of water by the efflux method has studied carefully the data of Poiseuille and Jacobson in the effort to find the value of m which would most nearly accord with the experimental results. Throwing Eq. (8) in the form

$$pt = \frac{8\eta Vl}{\pi g R^4} + \frac{m\rho V^2}{\pi^2 g R^4 t},\tag{9}$$

we observe that since for a given tube and liquid only p and t
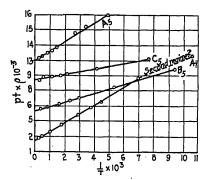
Fig. 2.—Finding the value of m for the kinetic energy correction.

vary, this is the equation of a straight line and may be written,

$$pt = a + \frac{b}{t}\tag{9a}$$

where a and b are constants. Plotting the values of $1/t$ as abscissas and of pt as ordinates Knibbs obtained the curves shown in Fig. 2, using the data for Poiseuille's tubes A^V, A^{VII}, B^V, and C^V. When t becomes very great the corrective term vanishes and $pt = a$. The values of a are given by the intercepts of the curves with the axis of ordinates. The tangent of the angle which a line makes with the axis of abscissas gives the value of b, from which the value of m is obtained, since

$$m = b\frac{\pi^2 g R^4}{\rho V^2}$$

Using a combination of numerical and graphical methods the following values were obtained.

TABLE VI.—VALUES OF m DEDUCED BY KNIBBS FROM POISEUILLE'S EXPERIMENTS

Tube	Length in centimeters	Mean radius in centimeters	Values of m
A^{III}...............	2.55	0.00708	1.04
A^{IV}...............	1.57	0.00708	1.02
A^{V}...............	0.95	0.00708	1.15
A^{VI}...............	0.68	0.00708	1.08
A^{VII}...............	0.10	0.00708	1.12
B...............	10.00	0.00567	1.23
B^{IV}...............	0.90	0.00567	1.14
B^{V}...............	0.39	0.00567	1.03
C^{V}...............	0.60	0.00427	1.87*
F^{I}...............	20.00	0.03267	1.08
F^{II}...............	9.97	0.03267	1.33
F^{III}...............	5.04	0.03267	1.16
F^{IV}...............	2.60	0.03267	0.82*
F^{V}...............	1.07	0.03267	0.82*

The mean is 1.14 or rejecting the values for C^V, F^{IV}, and F^V, 1.13. Certain of the tubes, *viz.*, A, A^I, A^{II}, B^I, B^{II}, B^{III}, C, C^I, C^{II}, C^{III}, C^{IV}, D, D^I, D^{II}, D^{III}, D^{IV}, E, E^I, E^{II}, and F give no satisfactory indication of the value of m. Knibbs deduced the value of m from 34 series of experiments made by Jacobson and obtained an average value of 1.14. This seems like a remarkable justification of the deduction of Boussinesq. But it should be added that the individual values vary from 0.82 to 1.44, yet perhaps this variation in the values of m should not be over-emphasized since in some instances the amounts of the corrections are much smaller than the discrepancies among the observations themselves. Knibbs thinks that the values do vary more than can possibly be accounted for by the experimental error and that possibly the value of m is not a constant for all instruments. It is highly desirable that further experiments be undertaken to determine whether m is a constant and equal to 1.12 or if it is not constant, the manner of its variation.

To the present writer it seems probable that the kinetic energy correction is truly constant for all tubes which are perfect cylinders. Irregularities in the bore of the tubes will, however, have very great influence in altering the amount of the correction, since the correction, *cf.* Equation (7), depends upon the fourth power of the radius of the tube. The shape of the ends of the capillary has already been referred to in this connection, but it seems preferable to consider the effect of the shape of the ends of the tube as quite distinct from the kinetic energy correction.

There has been a tendency among many recent experimenters to overlook the kinetic energy correction altogether, which is quite unjustifiable. We have indicated that it is not practicable to make the correction negligible. The only course open seems therefore to be to select a capillary which has as nearly as possible a uniform cylindrical (or elliptical) cross-section, to assume that m for such a tube has the constant value of 1.12, but to arrange the conditions of each experiment so that the kinetic energy correction will not exceed 1 or 2 per cent of the viscosity being measured. In this case an error of several per cent in the value of the constant will not affect the result, unless an accuracy is desired which is higher than has yet been attained. If such an accuracy is desired the value of m should be found for each tube by the method of Knibbs which has been discussed above, or by the method employed by Bingham and White (1912), which will be described below in discussing the alteration in the lines of flow at the ends of the tube.

Correction for Phenomena of the Flow Peculiar to the Ends of the Tube.—If two tubes of large diameter are
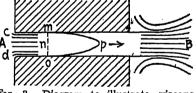
FIG. 3.—Diagram to illustrate viscous flow.

connected by a short capillary, the lines of flow will be as represented in Fig. 3, the direction of flow being readily visible in emulsions, suspensions, or when a strongly colored liquid is allowed to flow out from a fine tube in the body of colorless liquid near the entrance to the capillary, as was done by Reynolds (1883). In the reservoir at the entrance A there is apparently no disturbance until the opening of the capillary is

almost reached, and there the acceleration is very rapid. Even when the stream lines in the main part of the capillary are linear, it seems theoretically necessary to assume that there is a choking together of the stream lines near the entrance as indicated at *c*. It has been suggested that this effect might be prevented by using rounded or trumpet-shaped openings as indicated at *d*.

At the exit of the capillary, the stream continues on into the reservoir *B* for a considerable distance with its diameter apparently unchanged. However the fall in pressure of the liquid passing through the large tube *B* is negligible, so that the flow observed just beyond the exit takes place at the expense—not of pressure—but of kinetic energy taken up at the entrance. There is no distortion of the stream lines just within the exit end of the capillary, and it is not clear that any correction at this end is necessary, under the conditions which we have depicted. If the capillary opens into the air, there will naturally be a capillarity correction and the shape and material of the end of the tube will be of importance—*cf.* Ronceray (1911).

That the stream should continue for some distance beyond the exit with apparently constant diameter seems at first sight quite surprising, as one might suppose that the stream would at once drag along the adjacent fluid. The explanation is not far to seek. In the first place one should remember that the velocities even in the capillary are by no means uniform. Equation (3) tells us that particles which at a given moment are in a plane surface *mno* will after a certain time has elapsed be in a paraboloid surface *mpo*. The transition from the stationary cylinder of fluid in contact with the wall to the coaxial cylinders having high speed is *apparently* abrupt. As the exit of the capillary is passed, there is nothing to prevent the larger mass of liquid from being drawn along except its own inertia. But the rate at which the kinetic energy of the inner coaxial cylinders of fluid passes out into the outer cylinders is proportional to the viscosity of the medium and to the area of the cylinder. Thus in a fluid of low viscosity a capillary stream will penetrate for some distance. The stream disappears rather suddenly due probably to the development of eddies.

Couette has attempted to evaluate the effects of the ends of the tubes by supposing that they are equivalent to an addition to

the actual length of the capillary, which he represents by A.   The corrected viscosity η_c should therefore be calculated by the formula

$$\eta_c = \frac{\pi g p R^4 t}{8V(l+\Lambda)} - \frac{m\rho V}{8\pi t(l+\lambda)} \tag{10}$$

According to Couette the corrected viscosity is always a little smaller than that calculated by means of Eq. (8) and we obtain the relation

$$\frac{\eta}{\eta_o} = \frac{l+\Lambda}{l}$$

$$\Lambda = l\,\frac{\eta - \eta_o}{\eta_c}$$

Since A may be presumed to be the same for tubes of equal diameter but of unequal lengths l and l', one should obtain different viscosities η and η' by applying Eq. (8) to the same fluid. There would thus be the relation

$$\Lambda = l\,\frac{\eta - \eta_c}{\eta_o} = l'\frac{\eta' - \eta_c}{\eta_c} \tag{11}$$

To test out his theory, Couette used experimental results of Poiseuille with tubes A^{IV} and A^V which gave poor agreement with the simple law, Eq. (5) *cf.* Table II, VII and VIII.   The efflux times are given in column 1, the viscosities η_p calculated from the simple Poiseuille formula (5), in column 2, the more nearly correct viscosities η and η', calculated from Eq. (8) taking $m = 1.00$, in column 3.

TABLE VII.—VISCOSITY OF WATER CALCULATED FROM POISEUILLE'S
EXPERIMENTS WITH TUBE A^{iv}

For dimensions *cf.* Appendix D, Table I, p. 331

Time	η_p Eq. (5)	η Eq. (8), $m = 1.00$
8,646	0.01332	0.01328
4,355	0.01349	0.01339
2,194	0.01347	0.01332
1,455	0.01347	0.01324
1,116	0.01355	0.01325
571	0.01384	0.01325
298	0.01443	0.01330

TABLE VIII.—VISCOSITY OF WATER CALCULATED FROM POISEUILLE'S
EXPERIMENTS WITH TUBE A^v

For dimensions *cf.* Appendix D, Table I, p. 331

Time	η_p Eq. (5)	η' Eq. (8), $m = 1.00$
3,829	0.01383	0.01363
1,924	0.01404	0.01363
994	0.01442	0.01363
682	0.01479	0.01364
537	0.01512	0.01366
291	0.01651	0.01382
165	0.01863	0.01388

The values of η vary but little around the mean 0.01329, while the values of η_p show a regular progression, thus demonstrating the importance of the kinetic energy correction. The first three values of η' in Table VIII are constant and equal to 0.01363. The last four values show a steady increase which may be due to turbulent flow at such high velocities. From η and η', which are notably different in value, the corrected viscosity η_o as well as the value of Λ may be obtained by the use of Eq. (11). We get $\eta_o = 0.01303$ and $\Lambda = 0.041$ cm. The mean diameter of these tubes was 0.01417 cm hence, the fictitious elongation of the tube is a little less than three times the diameter $\left(\dfrac{\Lambda}{2R} = 2.868\right)$.

Couette also obtained the corrected viscosity directly by experiment, in a very ingenious manner. He employed two capillaries simultaneously, which had the same diameter but different lengths. The arrangement of his apparatus is shown in Fig. 4, where T_1 and T_2 are the two capillaries connecting three reservoirs M, N, and P. The pressure in each reservoir is measured on the differential manometer H. Since the volume of efflux through both capillaries is the same and may be calculated from the increase in weight of the liquid in the receiving flask D, we obtain from Eqs. (7) and (9) the relation

$$V = \frac{\pi g R^4 t(p_1 - p_k)}{8V\eta_o(l_1 + \Lambda)} = \frac{\pi j R^4 t(p_2 - p_k)}{8V\eta_o(l_2 - \Lambda)}$$

or

$$V = \frac{\pi g R^4 t}{8V\eta_o} \cdot \frac{p_1 - p_2}{l_1 - l_2}.$$

By thus eliminating the correction for the kinetic energy and the ends of the tubes, Couette obtained, for the corrected viscosity (η_o) of water at 10°, 0.01309 which is in excellent agreement with the value calculated above from Poiseuille's experiments.   If, on the other hand, the viscosity (η) is calculated by means of Eq. (8) with $m = 1.00$ for one of Couette's tubes, the apparent viscosity (η) is 0.01389.   From the values of η and η_o the value of Λ may be calculated as above.   It is 0.32 cm and the diameter
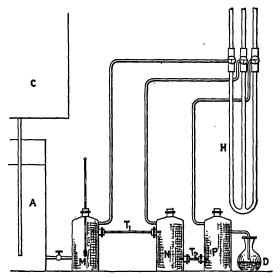
Fig. 4.—Capillary-tube viscometer.   Couette.

of the tube is 0.090 cm so that the fictitious length to be added is a little over three times the diameter of the tube.

In the experiments used by Couette to calculate the value of Λ the kinetic energy correction is very large, hence a considerable error may have been introduced by taking m as equal to 1.00 instead of the more probable 1.12.   Furthermore the range of data used in establishing his conclusion is rather limited. Hence, Knibbs has made an extended study of the same subject. If for Λ we substitute nR, Eq. (9) may be written

$$\frac{\pi g R^4}{8Vl}\left(p - \frac{m\rho V^2}{\pi^2 g l^2 R^4}\right) t = \eta_o\left(1 + \frac{nR}{l}\right)$$

but since from Eq. (9a) we have that

$$\left(p - \frac{m\rho V^2}{\pi^2 g t^2 R^4}\right) t = a$$

and therefore

$$\frac{\pi g R^4 a}{8 V l} = \eta_c \left(1 + \frac{nR}{l}\right).$$

This is the equation of a straight line. If values of $\frac{\pi g R^4 a}{8 V l}$ are plotted as ordinates and those of R/l as abscissas, the intercept on the axis of ordinates will give the corrected viscosity, *i.e.*, the value of the viscosity when $l = \infty$ or $R = 0$; and the tangent of the angle made by the line with the axis of abscissas when divided
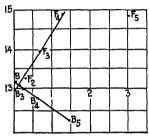
Fig. 5.—Finding the value of n for the "end correction."

by the viscosity will give the factor n required. Figure 5, taken from Knibbs' work, illustrates the method as applied to the tubes used by Poiseuille B to B^V and F to F^{IV}. The values of n are found to be -5.2 and $+11.2$ respectively. According to Knibbs "these results challenge the propriety of Couette's statement that Λ may be always regarded as positive and taken as nearly three times the diameter of the tube." In order to adequately test the question Knibbs took the whole series of Poiseuille's experiments at $10°$ and reduced them rigorously on the basis of Eq. (8) taking into account the peculiarities of the bore of the tubes used by Poiseuille as indicated in his data. Whenever possible the value of pt (*cf.* Eq. (9)) was obtained by extrapolation since then the correction term vanishes; in the other cases marked with a star, the value of m was taken as 1.12. The results are arranged according to increasing values of R/l, since if n has a positive value there should be a progressive increase in the values of the viscosity.

Rejecting the last four values as uncertain, the general mean is 0.013107 which is almost identical with the mean for each group of eight, whereas if n had a constant value there should be a steady progression. On the other hand the values for the viscosity for the B series of tubes increase while those for the F series decrease as we go down the Table. It appears therefore that no general value can be assigned to n unless it be zero.

TABLE IX.—THE VISCOSITY OF WATER AT 10° CALCULATED BY KNIBBS FROM
POISEUILLE'S EXPERIMENTS, USING EQ. (8)

Tube	$\frac{R}{l} \times 10^5$	$R^4 \times 10^{10}$	η
D................	22	0.242840	0.013074*
M................	37	0.002367	0.013090*
C................	42	3.250400	0.013028*
D^I................	44	0.233770	0.013020*
B................	56	10.235000	0.013202
C^I................	57	3.265900	0.013071*
E................	64	0.047160	0.013242*
A................	70	24.941000	0.013145
		Mean..........	**0.013109**
B^I................	75	10.276000	0.013134*
F................	85	11,207.000000	0.013147
C^{II}................	86	3.298000	0.013151*
D^{II}................	87	0.227870	0.013078*
A^I................	93	25.059000	0.013109*
B^{II}................	115	10.303000	0.013070*
A^{II}................	139	25.183000	0.013119*
F^I................	163	11,187.000000	0.013065
		Mean..........	**0.013109**
E^I................	174	0.048400	0.013588*
C^{III}................	175	3.339400	0.013092*
D^{III}................	219	0.224400	0.013045*
B^{III}................	240	10.331000	0.013002*
A^{III}................	277	25.231000	0.012946
F^{II}................	326	11,233.000000	0.013249
C^{IV}................	421	3.339400	0.012498*
A^{IV}................	450	25.231000	0.013343
		Mean..........	**0.013095**
M^I................	558	0.002367	0.013181*
B^{IV}................	630	10.357000	0.012742
F^{III}................	646	11,290.000000	0.013967
D^{IV}................	649	0.223310	0.012652*
E^I................	706	0.048400	0.013222*
C^V................	709	3.339400	0.012015
A^V................	742	25.231000	0.013515
A^{VI}................	1,046	25.231000	0.013607
		Mean..........	**0.013113**
F^{IV}................	1,254	11,316.000000	0.014891
B^V................	1,455	10.368000	0.012193
F^V................	3,034	11,316.000000	0.014851
A^{VII}................	7,088	25.231000	0.016980

Bingham and White (1912) have confirmed the conclusion of Knibbs by a study of interrupted flow. A capillary $l = 9.38$ cm $R = 0.01378$ cm was used to determine the time of flow of a given volume of water at 25° under a determined pressure. The capillary was then broken squarely in two and the parts separated by glass tubing, the whole being afterward covered with stout rubber tubing. The time of flow was again determined under the same conditions as before except that the corrections for kinetic energy and for the effects of the ends of the tubes were doubled by the interruption in the flow. The breaking of the capillary was then repeated until the capillary was in six parts, the corrections necessary being proportional to the number of capillaries. For this case Eq. (10) becomes

$$\eta_o = \frac{\pi g R^4 p t}{8V(l + b\Lambda)} - \frac{m\rho V b}{8\pi t(l + b\Lambda)}$$
$$= C \frac{pt}{l + b\Lambda} - C' \frac{mb}{l + b\Lambda} \tag{12}$$

where C and C' are constants under the conditions of experiment, and b is the number of capillaries, and Λ as before is the fictitious length to be added to each capillary. Substituting in Eq. (12) the values of the time of efflux and the pressure when the capillary is unbroken t_1 and p_1 and when broken t_2 and p_2 respectively, we obtain the relation

$$\frac{l + b\Lambda}{l + \Lambda} = \frac{Cp_2t_2 - C'mb/t_2}{Cp_1t_1 - C'm_1/t_1} = K$$

hence,

$$\Lambda = \frac{K - 1}{b - K} l.$$

TABLE X.—EXPERIMENTS TO DETERMINE THE "FICTITIOUS LENGTH" OF A CAPILLARY UNDER CONDITIONS OF INTERRUPTED FLOW

Number of capillaries b	Time	Pressure in grams per cm²	$Cpt - \dfrac{1.12C'b}{t}$	K	Λ
1	179.7	87.46	0.0836		
2	180.2	87.77	0.0837	1.00	1+0.009
3	182.4	87.32	0.0835	0.99	9−0.006
4	183.1	87.75	0.0836	1.00	0 0.000
6	185.0	88.25	0.0838	1.00	2+0.003

Since the values of K are unity within the experimental error the addition to the length is zero. In no single instance does the value of Λ amount to even one-half the diameter of the tube. If however the value of m had been taken as unity, Λ would have appeared to have positive value.

Had Λ been found to have a definite value, it would have been necessary to consider the legitimacy of making the correction by means of an addition to the length of the capillary instead of by means of a correction in the pressure as suggested in Eq. (2), but since no definite value can be assigned to this correction, there is no need for raising the question.

The shape of the ends of the tube are of considerable importance in determining the development of turbulent flow, under certain conditions. Tubes with trumpet-shaped entrances appear to promote linear flow (*cf.* Reynolds (1883) and Couette (1890) p. 486).

Slipping.—Coulomb (1801) made experiments with an oscillating disk of white metal immersed in water, and he noted that coating the disk with tallow or sprinkling it over with sandstone had no effect upon the vibrations. This seemed to prove that the fluid in contact with the disk moved with it, and that the property being measured was characteristic of the fluid and not of the nature of the surface. These observations were confirmed by O. Meyer in 1861.

After the Law of Poiseuille had been experimentally and theoretically established, it was still unsatisfactory that the results of measurements of viscosity by the efflux method did not agree with those by other methods. It was natural to suppose that the discrepancy might be explained by the external friction between the fluid and the solid boundary which had been assumed by Navier (1823), *cf.* also Margules (1881) and Hadamard (1903). Helmholtz in his derivation of the Law of Poiseuille had taken into account the effect of slipping and obtained the formula, which in our notation is

$$V = \frac{\pi p g t}{8 \eta l}\Big[R^4 + 4\lambda R^3 \Big] \tag{13}$$
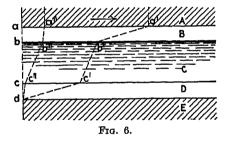
where λ depends upon the nature of the fluid as well as upon that of the bounding surface. In treatises on hydrodynamics this is usually written

$$V = \frac{\pi g p t}{8 \eta l}\Big[R^4 + 4\frac{\eta}{\beta} R^3 \Big]$$

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β being the coefficient of sliding friction which is the reciprocal of the coefficient of slipping.

From the experiments of Piotrowski upon the oscillations of a hollow, polished metal sphere, suspended bifilarly and filled with the viscous liquid, Helmholtz deduced a value for λ of 0.23534 for water, but it is worth noting that he deduced a value of the viscosity which was about 40 per cent greater than that obtained by the efflux method. From some efflux experiments of Girard (1815) using copper tubes, Helmholtz deduced the value $\lambda = 0.03984$. More recently Brodman (1892) has experimented with concentric metal spheres and coaxial cylinders, the space between being filled with the viscous substance. He thought that he found evidence of slipping.

Slipping can be best understood in cases where a liquid does not wet the surface, as is true of mercury moving over a glass surface. If we consider a horizontal glass surface A, Fig. 6, as being moved tangentially toward the right over a surface E,

Fig. 6.

between which there is a thin layer of mercury C, then we can imagine that the mercury is separated from the glass on either side by thin films B and D of some other medium, usually air. Points in a surface at right angles to the above indicated by $abcd$ may at a later time occupy the relative positions $a'b'c'd$ or if the films B and D are more viscous than the mercury the section may be better represented by $a''b''c''d$. But from Eq. (1)

$$dv \propto \varphi ds$$

so that in any case, the respective contributions to the flow by the inner mercury layer or by the superficial films will depend upon their relative fluidities and their relative thicknesses. Whether the liquid wets the surface or not, anything which affects the

fluidity of the surface film, whether it be surface tension, absolute pressure, positive or negative polarization, static electricity, or magnetism may therefore affect the amount of flow. And these effects when detected experimentally would undoubtedly be attributed to slipping or to the overcoming of external friction. So while we might expect the effect of slipping to be more pronounced in cases where the liquid does not wet the surface, it is quite possible that even when the liquid does wet the surface, the fluidity of the liquid near the surface is not identical with that within the body of the liquid.

On the other hand, it is important to remember that the thickness of the layer of liquid affected by the forces of adhesion, with which we are here chiefly concerned, is only molecular. Even with mercury in a glass tube, the thickness of the layer of air seems to be of molecular dimensions. One may get an idea of the upper limit to this thickness by the following experiment. A thread of mercury was placed in a narrow capillary so that the air surface would be relatively large. Taking care that no air-bubbles were present, the length of the thread was measured with a dividing engine, in a determined part of the tube. The tube was exhausted from both ends simultaneously and the thread moved back and forth in order to sweep out the supposed layer of air. When the mercury was finally brought back to its former position no decrease in length could be detected. *In order to have slipping under ordinary conditions of measurement it would appear that the surface film must be of very much more than molecular thickness or else it must have practically infinite fluidity.* In view of the strong adhesion[1] between all liquids and solids it seems improbable that the particular layer of liquid in contact with the solid should show an amount of flow which is comparable in amount with that of all of the other practically infinite layers of liquid.

Nevertheless if the value deduced by Helmholtz for water on a metal surface be correct, $\lambda = 0.23534$, the effect of slipping ought to be readily observed. According to Whetham (1890), if we take $R = 0.051$, Eq. (12) becomes

$$V = \frac{\pi p g}{8 \eta l} \, 117.67 \times 10^{-6}$$

[1] *Cf.* Duclaux, 1872.

whereas if there were no slip and therefore $\lambda = 0$ we would have

$$V = \frac{\pi p g}{8 \eta l} \, 6.25 \times 10^{-6}$$

Thus it would appear that the rate of flow through a polished metal tube should be nearly 20 times more rapid than through a tube in which there is no slip. Since Poiseuille's experiments prove that the viscosity is constant for tubes of very different radius when calculated without regard to slipping, there can be no slipping when water flows through glass tubes. This conclusion is admitted by Helmholtz.

Jacobson (1860) criticised Helmholtz's use of Girard's experiments in that he failed to apply any correction to the pressure. Jacobson himself experimented with copper tubes as well as glass tubes but found no evidence of slipping.

Warburg (1870) investigated the flow of mercury in glass tubes. He found that Poiseuille's law of pressures and his law of diameters were verified, which proved that slipping did not occur. Bénard as reported by Brillouin (1907) page 152, has repeated the work of Warburg using greater care, and he finds that λ cannot have a value greater than 0.00001.

Whetham (1890) caused water to flow through a glass tube before and after being silvered, proper corrections being made for changes in temperature and in the radius of the tube, due to the silver layer. Different thicknesses of silver as well as different pressures were used, but the difference in the times of flow between the silvered and unsilvered tubes were all within the limit of experimental error. Copper tubes were also used and the results in all cases were in agreement with Poiseuille's observations. Cleaning the tubes with acids and alkalies, polishing with emery powder, coating with a film of oil and amalgamating with mercury were all without effect in producing a deviation which could be detected. Whetham repeated an experiment of Piotrowski with an oscillating glass flask, plain and silvered. Care was taken to make correction for temperature and to prevent changes in the bifilar suspension which seems to have been neglected by Piotrowski. Whetham found the ratio of the friction of water on glass to the friction of water on silver to be 1.0022, which may be taken as unity within the limits of experimental error. Couette (1888–1890) attacked the problem

independently but along much the same lines. He tried the effect of a layer of grease and of silver on the inside of a tube. He found invariably the same efflux time or even a little greater which was due to the diminution in the radius of the tube. But even this latter effect did not occur when the thickness of the silver layer was a negligible fraction of the radius of the tube. He then used tubes of white metal, copper, and paraffin using rates of efflux close to the critical values, and obtained the following results:

TABLE XI.—COUETTE'S EXPERIMENTS ON SLIPPING

Substance of tube	Temperature	η Observed	η Calculated from Poiseuille
Copper.............	15.5	0.01175	0.01130
Copper...........	17.3	0.01073	0.01079
White metal......	18.2	0.01037	0.01055
White metal......	18.9	0.01064	0.01037
White metal......	18.3	0.01092	0.01052
Paraffin..........	12.6	0.01241	0.01219
Paraffin..........	12.9	0.01278	0.01209
Paraffin..........	12.3	0.01276	0.01228

Couette goes further and gives reasons for the conclusion that slipping does not occur even after the flow becomes turbulent.

More recently Ladenburg (1908) has carefully repeated the experiments of Piotrowski under as nearly as possible the same

TABLE XII.—LADENBURG'S EXPERIMENTS WITH AN OSCILLATING GLASS FLASK, SHOWING ABSENCE OF SLIPPING, AT 19.0°

Flask	Logarithm decrement	Period of vibration	Remark
A................	0.019570 ± 2	$11,973 \pm 2$	Unsilvered
A................	0.019642 ± 3	$12,049 \pm 2$	Silvered
A................	0.019620 ± 3	$11,990 \pm 1$	Unsilvered
B................	0.025026 ± 25	$11,716 \pm 4$	Unsilvered
B................	0.025011 ± 15	$11,688 \pm 2$	Silvered
C................	0.025162 ± 2	$11,870 \pm 2$	Silvered

experimental conditions. He used plain and silvered oscillating glass vessels and a hollow metal sphere. Table XII proves conclusively that slipping was absent in the former case.

Using the hollow metal sphere filled with water, Ladenburg obtained values of the viscosity which agree with the values found by other methods, and shown in Table XIII.

TABLE XIII.—A COMPARISON OF THE VISCOSITY OF WATER AS OBTAINED BY DIFFERENT METHODS (LADENBURG)

Method	η at 17.5°	η at 19.2°	Observer
Efflux glass...............	0.01076	0.01031	Poiseuille (1846)
Efflux glass..............	0.01065	0.01027	Sprung (1876)
Efflux glass...............	0.01075	0.01030	Slotte (1883)
Efflux glass...............	0.01067	0.01025	Thorpe and Rodger (1894)
Oscillating solid sphere.....	0.01099	0.01054	W. König (1887)
Oscillating hollow cylinder..	0.01082	0.01037	Mützel (1891)
Oscillating hollow sphere...	0.01065	0.01032	Ladenburg (1908)

Ladenburg indicates how Helmholtz erroneously obtained his large coefficient of slipping by overlooking a point in the theory, and recalculating Piotrowski's data he finds that instead of the viscosity being 40 per cent greater than the generally accepted value, this difference becomes only 3 per cent and the slipping becomes negligible.

It was stated above that the verification of the Law of Diameters of Poiseuille is a proof that slipping does not occur between glass and water. Knibbs (1895) has collected an extensive table of observations of the viscosity of water at 10° for tubes of various materials having radii varying from 0.0140 to 0.6350 cm or nearly a thousand-fold, but there is no evidence of progressive deviation as the radius increases.

In experimenting on the possible effect of an electrical or magnetic field upon viscosity, W. König (1885) obtained a negative result. Duff (1896) seemed to detect an increase in the viscosity of castor oil of 0.5 per cent using the falling drop method and a potential gradient of 27,000 volts per centimeter, but for the most part the results were negative. Quincke (1897)

found a definite effect on the viscosity in an electrical field, which Schaufelberger (1898) attempted to explain on the basis of hysteresis. However, Pacher and Finazzi (1900) obtained results which were contrary to those of Duff and Quincke finding that insulating liquids under the action of an electrical field do not undergo any sensible change in viscosity. Ercolini (1903) made experiments along the same line and concluded that the effect was less than his experimental error. He used petroleum, benzene, turpentine, olive oil, and vaseline. Carpini (1903) measured the viscosity of magnetic liquids in a magnetic field but found no certain effect. Koch (1911) tried the effect of oxygen or hydrogen polarization at the boundary using a platinum tube and an oscillating copper disk. No change in the viscosity was observed and Koch regards this as strong evidence against slipping. Ronceray (1911) has studied the effect of surface tension.

These results seem to make it quite certain that, whether the liquid wets the solid or not, there is no measurable difference between the velocity of the solid and of the liquid immediately in contact with it, at least so long as the flow is linear.

The Transition from Linear to Turbulent Flow.—It is well known that the formulas which have been discussed do not apply to the ordinary flow of liquids in pipes. Under ordinary conditions we know that the flow is undulatory, instead of being linear as is assumed in the simple laws of motion. It is important that we know under what conditions these sinuous motions appear so that they may be properly taken into account or guarded against. An extended study of the flow of water in pipes having a diameter varying from 0.14 to 50 cm was made by Darcy (1858). He found the hydraulic resistance proportional to I^n where n had a value nearly equal to 2 (1.92). He saw more clearly than any of his predecessors that hydraulic flow is very different in character from the viscous flow studied by Poiseuille, since the viscous resistance is proportional to the first power of the mean velocity (I). Darcy paid little attention to the temperature at which his experiments were carried out, probably as Reynolds remarks, because "the resistance after eddies have been established is nearly, if not quite, independent of the viscosity." Since Darcy's work was approved by the Academy

in 1845, he is probably the first to distinguish clearly between
the two régimes.

Hagen (1854) investigated the effect of changes in temperature
upon the rate of efflux in tubes of moderate diameters.   Figure 7
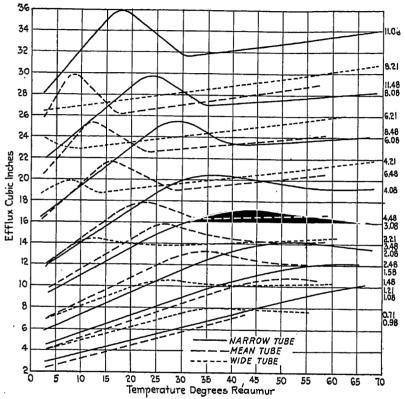
Fig. 7.—Transition from linear to turbulent flow.   The effect of temperature.

exhibits the results of his experiments.   The abscissas are
degrees, Reaumur, the ordinates the volumes in cubic inches
("Rheinland Zollen") transpiring in a unit of time.   The pressure
to which each curve corresponds is given at the right of the figure,
being expressed in inches of water.   Hagen used three tubes of
varying width as follows:

Tube	Radius, inches	Length, inches
Narrow...............	0.053844	18.092
Mean.................	0.077394	41.650
Wide.................	11.391400	39.858
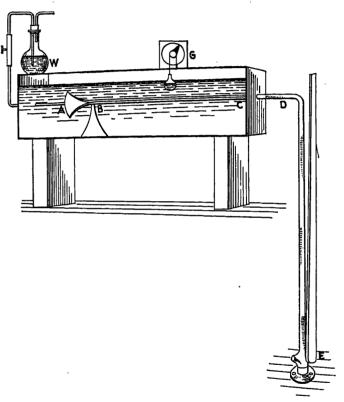
FIG. 8.—Apparatus of Reynolds for studying the critical régime.

Inspection of the figure shows that with the lowest pressure and the smaller tubes the efflux is a linear function of the temperature except at the highest temperatures. With the wide tube, however, there is a maximum of efflux at about 37° even at the smallest pressure. As the pressure is increased the maximum appears at a

lower and lower temperature and the maximum appears even in the smallest tube used. There is a minimum of efflux after passing the maximum but then the efflux becomes again a linear function of the temperature. Brillouin (1907) page 208, has confirmed the experimental results of Hagen.

A clear picture of the phenomena connected with the passage from one régime to the other has been given by Reynolds (1883). One form of apparatus used by him is depicted in Fig. 8. It
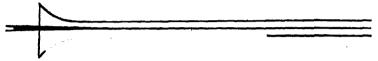
Fig. 9.—Linear flow.

consists of a glass tube *BC*, with a trumpet-shaped mouthpiece *AB* of wood, which was carefully shaped so that the surfaces would be continuous from the wood to the glass. Connected with the other end is a metal tube *CD* with a valve at *E* having an opening of nearly 1 sq. in. The cock was controlled by a long lever so that the observer could stand at the level of the bath, which surrounded the tube *BC*. The wash-bottle *W* contained a colored liquid which was led to the inside of the trumpet-shaped opening. The gage *G* was used for determining the level

Fig. 10.—The beginning of turbulent flow.

of water in the tank. When the valve *E* was gradually opened and the color was at the same time allowed to flow out slowly, the color was drawn out into a narrow band which was beautifully steady having the appearance shown in Fig. 9. Any considerable disturbance of the water in the tank would make itself evident by a wavering of the color band in the tube; sometimes it would be driven against the glass tube and would spread out, but without any indication of eddies.

As the velocity increased however, suddenly at a point 30 or more times the diameter of the tube from the entrance, the color

band appeared to expand and to fill the remainder of the tube with a colored cloud. When looked at by means of an electric spark in a darkened room, the colored cloud resolved itself into distinct eddies having the appearance shown in Fig. 10. By lowering the velocity ever so slightly, the undulatory movement would disappear, only to reappear as soon as the velocity was increased. If the water in the tank was not steady the eddies appeared at a lower velocity and an obstruction in the tube caused the eddies to be produced at the obstruction at a considerably lower velocity than before. "Another phenomenon which was very marked in the smaller tubes was the intermittent character of the disturbance. The disturbance would suddenly come on through a certain length of the tube, pass away, and then come again, giving the appearance of flashes, and these flashes would often commence successively at one point in the pipe." The appearance when the flashes succeeded each other rapidly is shown

Fig. 11.—Flashing.

in Fig. 11. "This condition of flashing was quite as marked when the water in the tank was very steady, as when somewhat disturbed. Under no circumstances would the disturbance occur nearer the funnel than about 30 diameters in any of the pipes, and the flashes generally, but not always commenced at about this point. In the smaller tubes generally, and with the larger tube in the case of ice-cold water at 4°, the first evidence of instability was an occasional flash beginning at the usual place and passing out as a disturbed patch 2 or 3 in. long. As the velocity further increased these flashes became more frequent until the disturbance became general."

Reynolds further noted that the free surface of a liquid indicates the nature of the motion beneath. In linear flow, the surface is like that of *plate glass*, in which objects are reflected without distortion, while in sinuous flow, the surface is like that of *sheet glass*. A colored liquid flowing out into a vessel of water has the appearance of a stationary glass rod in the first régime, but as the

velocity is increased the surface takes on a sheet glass appearance due to the sinuous motions, and finally the stream breaks into eddies and is lost to view (*cf. Collected Papers* 2, 158).

Reynolds reasoned from the equations of motion that the birth of eddies should depend upon a definite value of

$$\rho R I \varphi$$

where R is a single linear parameter, as the radius of the tube, and I is a single velocity parameter, as the mean velocity of flow along the tube. Reynolds found the value of the constant to be approximately 1,000, hence, the maximum mean velocity in centimeters per second for which we may expect linear flow, may be taken to be

$$I = \frac{1,000}{\rho R \varphi} \tag{14}$$

In Table XIV we have calculated the value of the product $\rho R I \varphi$ from some of Reynolds' observations near the critical velocity.

TABLE XIV.—CALCULATION OF THE CRITICAL VELOCITY CONSTANT

Flow	Temperature	ρ	R centimeters	φ	I centimeters per second	$\rho R I \varphi$
Steady......	9	1.00	0.3075	74.4	44.26	1,012
Unsteady...	8	1.00	0.3075	72.4	48.65	1,113
Steady......	5	1.00	0.3075	66.2	51.06	1,039
Unsteady...	5	1.00	0.3075	66.2	54.33	1,106
Steady......	8	1.00	0.6350	72.4	22.60	1,039
Unsteady...	8	1.00	0.6350	72.4	22.60	1,039

Reynolds tried plotting the mean velocity against the fall in pressure per unit length of the tube as shown in Fig. 12. It is to be observed that the resistance increases as a linear function of the velocity according to Poiseuille's law up to a certain definite point, and that from that point on the resistance varies as some higher power of the velocity. This power as we shall see is constant and is, according to Reynolds equal to 1.723 over a wide range of pressures. Formulated this relation becomes

$$P = K I^n \tag{15}$$

where P is the pressure gradient and n is the constant. In the first régime $n = 1$ and we have

$$P = KI$$

It may be remarked here that hydraulicians have usually
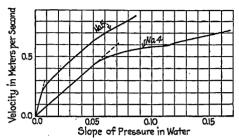
FIG. 12.—Efflux-shear curves passing through the critical régime.
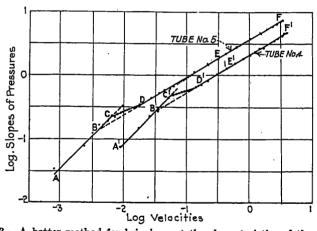
FIG. 13.—A better method for bringing out the characteristics of the viscous, hydraulic, and critical régimes.

employed the expressions

$$P = KI^2$$

or

$$P = AI + BI^2$$

Putting Eq. (15) in the form

$$\log P = n \log I + \log K$$
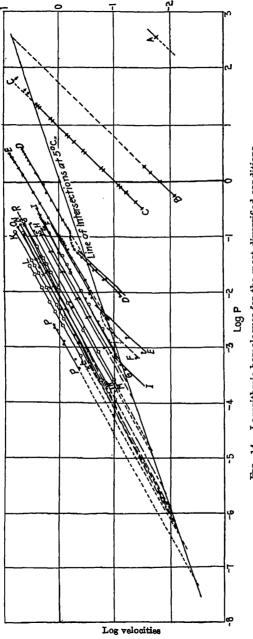
we observe that the relations may be presented more forcefully by plotting the logarithms of the pressure gradients as abscissas

and the logarithms of the mean velocities as ordinates. For tubes 4 and 5, Reynolds obtained the curves given in Fig. 13. Linear flow exists along the line ABC, or $A'B'C'$, the hydraulic régime exists along the line $BDEF$ or $B'D'E'F'$. It is evident now that n is constant for each part of the curves for the two tubes and that it is the same for both, *i.e.* the curves can be exactly superimposed by merely a rectangular shift. The line ABC is inclined at an angle of $45°$ so that $n = 1$, and the line $BDEF$ is inclined at an angle $30°-8'$ so that $n = 1.723$. Except for the unstable region BCD, the formula $P = KI^n$ will represent the viscosity in both régimes, it being necessary to merely change the value of n in passing from one régime to the other.

In passing from B to C it is evident that the linear flow becomes increasingly unstable, and thus is explained why the eddies appear suddenly and full-fledged, when the disturbance is sufficiently great. The more undisturbed the liquid is, the farther is it possible to go from B.

The points along the curve CD (or $C'D'$) correspond to the mixed régime where the flashing occurs, the turbulent movement alternating with the linear. Light has been thrown upon the cause of the flashing by Couette (1890) and Brillouin (1907), using a horizontal tube opening directly into the air. At high pressures the surface of the jet had a sheet-glass appearance indicating that the flow was hydraulic but the amplitude of the jet was constant. As the pressure was lowered the velocity fell to a point where linear flow began. But as the resistance was much less in linear flow, the velocity increased as shown by the increased amplitude of the jet, and the condition of hydraulic flow was reestablished. The rapidity of these fluctuations gradually increased as the pressure was further reduced, passed through a maximum and gradually declined as the linear flow came to predominate. Finally the jet became regular with a plate glass surface.
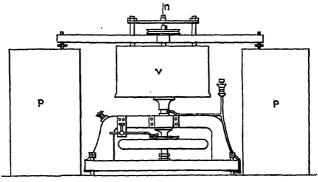
It has been suggested that there are really three régimes, one for velocities with which only linear flow can exist, a second for velocities with which only turbulent flow can exist, and a third where linear and turbulent flow alternate. The linear régime is sharply marked off from the hydraulic régime by the point B where the lines ABC and BDE intersect. While the period of

Fig. 14.—Logarithmic homologues for the most diversified conditions.

Log velocities

Number	Diameter	Temper-ature	Surface
A................	0.0014	10	Glass ⎫
B................	0.0270	10	Glass ⎬ Poiseuille
C................	0.0650	10	Glass ⎭
D................	0.615	5	Lead No. 4 ⎫ Reynolds
E................	1.270	5	Lead No. 5 ⎭
F................	1.400	..	Lead ⎫
G................	2.700	..	Lead
H................	4.100	..	Lead
I................	2.600	12	Varnished
J................	8.260	21	Varnished
K................	19.600	..	Varnished
L................	28.500	21	Varnished ⎬ Darcy
M................	8.190	15	Cast iron, new
N................	13.700	15	Cast iron, new
O................	18.800	..	Cast iron, new
P................	50.000	..	Cast iron, new
Q................	24.320	..	Cast iron, incrusted
R................	24.470	..	Cast iron, cleaned
S................	4.968	..	Glass ⎭

the oscillations in the mixed régime is entirely characteristic, it seems hardly probable that we can always sharply differentiate the mixed from the hydraulic régime. Indeed Couette (p. 486)

FIG. 15.—Coaxial cylinder viscometer of Couette.

found that with a tapering tube the oscillations do not appear at all. One may draw the conclusion from Reynolds' observations

that the formula $P = KI^n$ may be used in the critical régime.

Reynolds has compared the data of Darcy for large tubes, that of Poiseuille for small tubes, with his own, plotting the logarithmic homologues as in Fig. 13.   The result is shown in
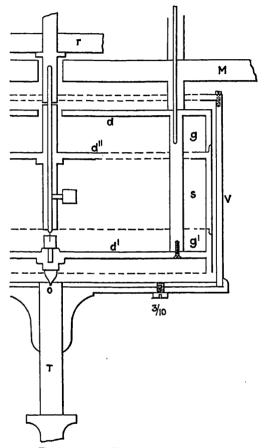
FIG. 16.—Detail of coaxial viscometer.

Fig. 14.   Each line represents the logarithmic homologue for some particular tube, described in the figure.   It is at once apparent that, for the most part, experiments have been made well below or else well above the critical values.   In the small tubes of Poiseuille the velocities were below the critical values.

The smallest tube with which he experimented, *A*, gives a curve, only part of which is shown in the figure.   It should be
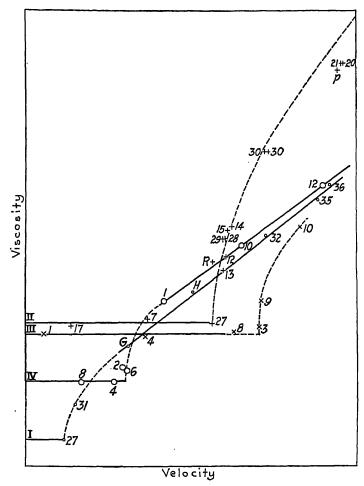
Fɪɢ. 17.—The transition from viscous to hydraulic flow with coaxial cylinders.

added that Reynolds corrected Poiseuille's data for the loss in kinetic energy.

For pipes ranging in diameter from 0.0014 to 500 cm and for pressure gradients ranging from 1 to 700,000, there is not a difference of more than 10 per cent in the experimental and

calculated velocities and, with very few exceptions, the agreement is within 2 or 3 per cent, and it does not appear that there is any systematic deviation.

Couette (1890) has strongly confirmed the work of Reynolds by his measurements with coaxial cylinders. The external appearance of the apparatus used is shown in Fig. 15 where V is the outer cylinder of brass which can be rotated at a constant velocity by means of an electric motor around its axis of figure T. The inner cylinder is supported by a wire attached at n. A section through a part of the apparatus in Fig. 16, shows the inner cylinder s while g and g' are guard rings to eliminate the effect of the ends of the cylinder. The torque may be measured by the forces exerted on the pulley r which are necessary to hold the cylinder in its zero position. Plotting viscosities as ordinates and the mean velocities as abscissas, he obtained Fig. 17. Curve I represents the results for the coaxial cylinders, curve II represents the same results on five times as large a scale in order to show better the point where the régime changes. Curves III and IV are for two different capillary tubes. It is clear from the figure that the viscosity is quite constant up to the point where the régime changes. The apparent viscosity then increases very rapidly, and finally becomes a linear function of the velocity. The dotted parts of the curves where the viscosity increases most rapidly, represents the region of the mixed régime, and the measurements were very difficult to obtain with precision.

He proved that $\rho R I \varphi = $ a constant by a series of experiments.

(1) The mean velocity at the lower limit of the oscillations is independent of the length of the tube. He used a glass tube $R = 0.1778$ and obtained the efflux per minute V', thus:

TABLE XV.—LAW OF LENGTHS

Length, centimeters	V' mean
86.5	388
71.5	367
57.9	365
41.8	376
25.7	394

(2) The mean velocity at the lower limit of the oscillations is inversely proportional to the radius of the tube.

TABLE XVI.—LAW OF RADII

R	Temperature	V'	$\dfrac{V'}{R}$
0.04998	12.7	103.6	2,073
0.09036	13.6	214.9	2,378
0.13070	13.6	344.0	2,632
0.17780	13.6	377.0	2,121
0.21080	13.6	542.0	2,570
0.27620	13.6	701.0	2,538
0.29690 (Copper)	15.0	648.0	2,182
0.45000	15.0	1,205.0	2,678

(3) The mean velocity at the lower limit of the oscillations is inversely proportional to the fluidity. For both mercury and water an elevation of the temperature caused a lowering of the mean velocity at the lower limit of the oscillations. The increase in the temperature causes an increase in the fluidity in both cases.

(4) Experiments with air and water confirm the law that the mean velocity at the lower limit of the oscillations is inversely proportional to the density of the medium. The number of turns of the outer cylinder per minute is taken as proportional to the mean velocity, a being a constant.

TABLE XVII.—LAW OF DENSITIES

Substance	η	ρ	aI	$a\varphi\rho I$
Water....	0.01096	1.0000	56	5,100
Air.......	0.00018	0.0012	800	5,300

There would be still some doubt whether the critical velocity is inversely proportional to the fluidity, but this doubt is removed by the work of Coker and Clement (1903) to test this very point. They used a single tube $l = 6$ ft. $R = 0.38$ in. measuring the flow of water over a range of temperatures from

4° to nearly 50°. Plotting the logarithmic homologues they obtained a family of curves exactly similar to those in Fig. 14, so that it is unnecessary to reproduce them. The points of intersections between the curves for linear and for turbulent flow lie on a perfectly straight line as is true in Fig. 14. This proves that the critical velocity is directly proportional to the viscosity. Indeed plotting the critical velocities read from their curves against the temperatures, one obtains a curve which is almost identical with that obtained by calculation from the viscosities according to the assumed law.

Compressible Fluids.—As a compressible fluid flows through a capillary under pressure, expansion takes place as the pressure is relieved. The expansion may give rise to several effects which must be taken into consideration. (1) The velocity increases as the fluid passes along the tube. (2) There must be a component of the flow which is toward the axis of the tube. (3) The expansion may cause a change of temperature. This may affect the flow in two ways (a) by changing the volume and consequently the velocity and (b) by changing the viscosity of the medium and consequently the resistance to the flow. (4) As the density changes, the viscosity may also change, unless the viscosity is independent of the density. (5) We must also consider whether the kinetic energy correction is changed when the velocity increases as the fluid passes along the tube.

For incompressible fluids, we have seen that the viscosity measurement may be made without reference to the absolute pressure. But with compressible fluids this is not the case, because the rate of expansion depends upon the absolute pressures, in the two reservoirs at the level of the capillary, P_1 and P_2. We will first suppose that Boyle's law holds, the flow taking place isothermally. For this case, as we shall see, page 243, the viscosity is independent of the density. Let U, P, and ρ represent the mean velocity, absolute pressure, and density at any cross-section of the tube. Since at any instant the quantity Q of the fluid passing every cross-section is constant, we have from Eq. (4)

$$Q = \rho U = \frac{\pi g R^4}{8\eta} \rho \frac{dp}{dl} = \frac{\pi g R^4}{8\eta} \frac{\rho}{2p} \frac{dP^2}{dl} \qquad (16)$$

But $\dfrac{\pi g R^4}{16\eta} \dfrac{\rho}{P}$ is constant and therefore $\dfrac{dP^2}{dl} = \dfrac{P_1{}^2 - P_2{}^2}{l}$

4

and we obtain

$$U = \frac{\pi g R^4}{16 l \eta} \cdot \frac{P_1{}^2 - P_2{}^2}{p} \tag{16a}$$

or

$$\eta = \frac{\pi g R^4 t}{16 l P_1 V_1}(P_1{}^2 - P_2{}^2) = \frac{\pi g R^4 t}{16 l P_2 V_2}(P_1{}^2 - P_2{}^2) \tag{17}$$

where V_1 and V_2 are the volumes corresponding to pressure P_1 and P_2.

Since $p = P_1 - P_2$ we observe that the ratio between the values of the viscosity calculated by Eqs. (17) and (5) is $\dfrac{P_1 + P_2}{2P}$ where P may have any value between P_1 and P_2 depending upon the value of V which is employed. If V be taken as

$$\frac{2P_1}{P_1 + P_2} V_1 = \frac{2P_2}{P_1 + P_2} V_2$$

(17) becomes identical with Eq. (5) and becomes unnecessary.

The derivation of the law for gases was made by O. E. Meyer (1866) and by Boussinesq (1868). With Fisher (1903) we may regard the above case where PV is constant as extreme, and that more generally we may take PV^n as constant. Equation (16) becomes on integration

$$U = \frac{\pi g R^4}{8 l \eta} \cdot \frac{P_1{}^{1 + \frac{1}{n}} - P_2{}^{1 + \frac{1}{n}}}{\left(1 + \dfrac{1}{n}\right) P^{\frac{1}{n}}}$$

When $n = \infty$ this becomes identical with Eq. (4), for incompressible fluids. When $n = 1$ the flow is isothermal and we obtain Eq. (16a). Ordinarily the value of n will lie between these two extremes, thus in adiabatic expansion $n = C_p/C_v = 1.0$ to 1.7, the ratio of the specific heats. Hence, it seems probable that the Law of Poiseuille as given in Eq. (5) may be used, irrespective of whether the fluid is compressible or not, but in every case the volume of flow must be taken as

$$V = \frac{\left(1 + \dfrac{1}{n}\right) P_1{}^{\frac{1}{n}} V_1}{P_1{}^{\frac{1}{n}} + P_1{}^{\frac{1}{n} - 1} P_2 + \ldots P_2{}^{\frac{1}{n}}} \tag{18}$$

In the extreme case where $n = 1$, if p is not greater than $P_2/10$

V will not differ from $\dfrac{V_1 + V_2}{2}$ by much over 0.2 per cent. This means that working at atmospheric pressure, with a hydrostatic pressure of over 100 cm of water, one may take the volume of flow as $\dfrac{V_1 + V_2}{2}$ without any very appreciable error. It is therefore extremely improbable that an appreciable error is incurred through our lack of knowledge in regard to the exact value of n in a given case. The effect of the temperature upon the viscosity will be discussed later, page 246, as a temperature correction.

The kinetic energy of the fluid increases as it passes along the tube, but we are interested only in the total amount of the kinetic energy as the fluid leaves the tube. This is $\pi \rho_2 R^2 I_2^3$. The total energy supplied in producing the flow is $\pi R^2 I_2 (P_1 - P_2)g$ and the difference between the two is the energy converted into heat $\pi R^2 I_2[(P_1 - P_2)g - q_2 I_2^2]$. The loss of head in dynes per cm^2 in imparting kinetic energy to the fluid is therefore

$$p_k g = P_2 I_2^2 = \frac{\rho_2 V_2^2}{\pi^2 R^4 t^2}$$

With this correction, but neglecting the slipping, we obtain

$$\eta = \frac{\pi g R^4 l}{8 V_2 l} \frac{P_1^2 - P_2^2}{2 P_2} - \frac{m \rho_2 V_2}{8 \pi l t} \tag{19}$$

Substituting V for V_2 and remembering that $\rho_2 V_2$ is constant, Eq. (19) becomes identical with the complete formula for the viscosity as given in Eq. (17).

Although it is admitted that the flow of compressible fluids is not quite linear, no correction for this has yet been attempted. However it is certain that the correction is negligible if p is small in comparison with P_2. The correction for slipping in gases plays an important part in the literature. The correction is the same as for incompressible fluids.

Turbulent Flow in Gases.—The distinction between viscous and turbulent flow in gases has been investigated by several workers, among whom we may mention particularly Grindley and Gibson (1908) and Ruckes (1908). Ruckes discovered that the criterion for gases was greatly raised if the capillary was blown out into a trumpet shape.

Plastic Flow or the Fourth Régime.—When a mixture of liquids, such as petroleum, is allowed to flow through a tube of large diameter filled with finely porous material like Fuller's earth, Gilpin[1] and others have shown that there is a tendency for the more volatile, *i.e.* the more fluid substances, to pass through the maze of capillaries first, leaving the more viscous substances behind. Naturally this effect is greatest when the pressure is very small. It is easy to see that under such conditions of flow the fluidity as calculated might appear quite abnormal. Just as the fluidity appears abnormal when the velocity exceeds a certain value and we pass into the second régime, so it appears that the fluidity may appear abnormal when the velocity drops below a certain critical value, and we pass into what may be called the "Fourth Régime."

With homogeneous liquids or gases of high fluidity it is difficult to work at excessively low velocities, particularly on account of the interference of dust particles. Very little work has been done upon such substances having low fluidity, so that for aught we know now the lower critical velocity may be observable only in mixtures.

Glaser (1907) measured the viscosity of colophonium-turpentine mixtures by the transpiration method with the object of testing the law of Poiseuille for very viscous and plastic substances. With one tube $R = 0.49$ cm, $l = 10.5$ cm he found

TABLE XVIII.—THE VISCOSITY OF AN 85 PER CENT COLOPHONIUM—15 PER CENT TURPENTINE MIXTURE AT 11.3° AND UNDER A CONSTANT PRESSURE OF 2,040 CM WATER IN TUBES OF VARIOUS DIAMETERS (GLASER)

R	l	t	V	$\eta \times 10^7$	$\varphi \times 10^{-8}$
1.525	25.1	600	2.28	4.20	2.38
1.019	15.9	1,800	2.30	4.21	2.37
0.746	16.0	900	0.329	4.25	2.35
0.576	15.1	18,000	1.972	4.22	2.36
0.364	15.8	46,800	0.755	5.22	1.80
0.257	15.2	43,200	0.149	6.59	1.51
0.158	15.1	173,500	0.023	19.90	0.50
0.117	15.4	3 weeks	0.000	∞	0.00

[1] *Am. Chem. J.*, **40**, 495 (1908); **44**, 251 (1910); **50**, 59 (1913).

the product of the pressure multiplied by the time of efflux to be constant. The velocities ranged from 0.00011 to 0.00175 cm per second. From these experiments Glaser concluded that "The velocity of efflux in this mixture is within very wide limits without influence upon the magnitude of the viscosity." But in experimenting with tubes of varying diameter, he obtained remarkable results a part of which are given in Table XVIII.

We observe with Glaser that the fluidity rapidly falls off as soon as the diameter falls below a certain limit. But this limit depends upon the fluidity of the mixture, as was proved
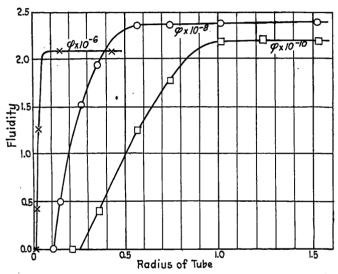
Fig. 18.—Eighty, eighty-five and ninety per cent mixtures of colophonium and turpentine give fluidities, multiplied by 10^{-6}, 10^{-8} and 10^{-10} respectively, which vary with the radius of the tube. Such mixtures are apparently *plastic* and do not obey the laws of viscous flow.

by working in the same way with 80 and 90 per cent colophonium mixtures, the true fluidities of which are approximately 2×10^{-6} and 2×10^{-10} respectively. Since with such rapidly increasing values, the viscosities are inconvenient to plot, we have changed his viscosities to fluidities. All of his values are plotted in Fig. 18, using apparent fluidities as ordinates and radii as abscissas. We note that the points lie, for the most

part, on a smooth curve indicating that the phenomenon under consideration is not one of mere clogging, as by accidental dust particles in ordinary measurements.   The effect is pronounced in a tube of about 0.8 cm radius with a 90 per cent colophonium mixture, but the effect is not noticeable in a tube of 0.1 cm radius with an 80 per cent mixture.   It is therefore no wonder if this effect is not noticeable in ordinary liquids which are millions of times yet more fluid.

The fact which seems to have been overlooked by Glaser and is of prime importance in explaining the phenomenon, is that the shearing stress and the mean velocity of efflux is very much less in the smaller tubes.   Obtaining the critical value of the radius for each mixture by the graphical method, we have calculated the mean velocity by means of Eq. (6).   It is of the same order of magnitude in all three cases being around 0.000,01 cm per second.   It seems probable that had these experiments been repeated at a very greatly different pressure, it would have been discovered that the viscosity is dependent upon the shearing force rather than upon the radius of the tube, and the conclusion that the viscosity is independent of the velocity would have been amended.   It is highly desirable that experiments be made to establish this point.

It is important to observe that each mixture used by Glaser gave a zero fluidity when the radius of the tube fell below a certain well-defined limit.   Bingham and Durham (1911) have studied various suspensions of clay, graphite *et cetera* in different liquids over a range of temperatures, using a single capillary and a nearly constant pressure.   As shown in Fig. 19, the fluidity-concentration curves are all linear and at all concentrations and temperatures they point to a well-defined mixture with zero fluidity, at no great concentration.   This mixture apparently sharply demarcates viscous from plastic flow, for be it noted that the mixture having "zero fluidity" was not a hard solid mass, but rather of the nature of a thin mud.   In the mixture of "zero fluidity" it appears that with the given instrument all of the pressure is required for some other purpose than to produce viscous flow.   The amount of pressure used up in this way is zero for the suspending medium alone but increases in a linear manner with the concentration of solid.   If this view is

correct, a part of the pressure is used up in producing plastic flow and the rest in producing viscous flow. If higher pressures
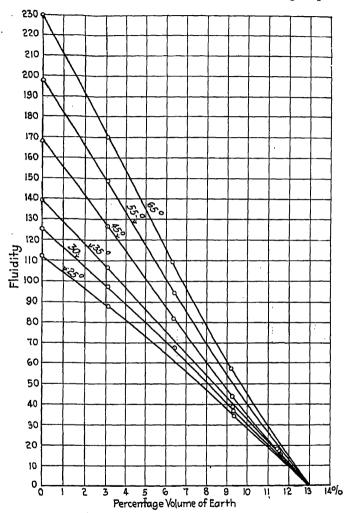
FIG. 19.—The fluidity of suspension of infusorial earth in water.

were used the zero of fluidity would be changed because there would be enough pressure to more than overcome the plastic resistance in the mixture that formerly had "zero fluidity."

Further work is therefore demanded in order that we may clearly define and separate the coefficients of plasticity and fluidity which are here measured together.

Surface Tension and Capillarity.—Several investigators have attempted to measure viscosity by means of a capillary opening directly into the air. Poiseuille (1846) found that whether drops were allowed to form on the end of the capillary or the end of the capillary was kept in contact with the wall of the receiving vessel, he was unable to obtain consistent results. The effect of surface tension varies with the rate of flow, with the temperature, and it also depends upon the shape and position of the end of the capillary, so that as a whole the effects are quite indeterminate. That the effects are large and variable, may be inferred from the measurements of Ronceray (1911) with a capillary, $l = 10.5$ cm, $R = 0.0275$, immersed under water or opening into the air, given in Table XIX.

TABLE XIX.—EFFECT OF SURFACE TENSION ON THE FLOW OF WATER (RONCERAY)

P centimeters, water	Time of flow of 10 ml in air at 17°	Time of flow immersed	Difference
10	1,132.0	1,089.44	42.6
20	559.5	550.4	9.1
30	373.0	368.5	4.5
40	280.6	277.4	3.2
50	224.9	222.7	2.2
60	187.9	186.1	1.8
70	161.8	159.5	2.3

Poiseuille recorded similar results. The irregularity is completely removed by having the end of the capillary immersed. Nevertheless in an apparatus like that used by Poiseuille there may still be a correction for capillary attraction within the bulb which is considerable (*cf.* p. 66).

Summary.—From the foregoing, it appears that under proper conditions, the only correction that it is necessary to make to the simple Law of Poiseuille is that for the kinetic energy of the fluid as it leaves the capillary $\dfrac{1.12\rho V}{8\pi lt}$. Other sources

of error such as surface tension, slipping at the boundary, necking in of the lines of flow at the entrance of the capillary, eddy currents inside of the capillary, resistance to flow outside of the capillary, peculiar shapes to the ends of the capillary affecting the magnitude of the kinetic energy correction have all been considered in detail. They may all be eliminated by using long, narrow capillaries with a low velocity of flow.

The fluidity of compressible fluids may be obtained by the same Law of Poiseuille but the volume of flow is approximately the mean of the volume at the entrance and at the exit of the capillary $\dfrac{V_1 + V_2}{2}$.

Plastic solids in their flow do not obey the Law of Poiseuille and their study is deferred until Chapter VIII. Many attempts have been made to measure the viscosity of soft solids. The fluidity of such a substance is not a constant quantity but falls off rapidly although regularly as the radius of the capillary falls below a certain point. This is not stoppage of the capillary of the ordinary sort due to extraneous particles, but rather a new type of flow. The terms fluidity and viscosity will therefore be avoided when referring to plastic substances in order to avoid confusion and a sharp criterion given by which a soft solid may be distinguished from a true fluid, just as Reynolds' criterion enables one to distinguish between viscous and turbulent flow.

CHAPTER IV

IS THE VISCOSITY A DEFINITE PHYSICAL QUANTITY?

So long as the theory was so imperfectly worked out that the values for the viscosity of a well-defined substance like water were different when obtained with different forms of instruments, it was inevitable that the whole theory and practice of viscosity measurement should have been called into question. Among numerous researches, we may cite in this connection those of Traube (1886), Wetzstein (1899) for liquids, Fisher (1909) for gases, and Reiger (1906) for solids. Since the limitations and corrections discussed in the preceding chapter have evolved very gradually, many of these researches are now of historical interest only, and their discussion here would be as tedious as it is unnecessary. Enough material has already been given to prove that viscosity is an entirely definite property for liquids. Table IX proved that tubes of quite diverse dimensions give entirely harmonious results. This has been confirmed repeatedly, especially by Jacobson, 1860, working with tubes of considerably larger bore. Not only are the results obtained with the transpiration method in agreement, among themselves, they also agree with the results from various other methods, as shown in Table XIII.

Knibbs (1896) has made a critical study of the existing data for water, recalculating and using the corrections suggested in the last chapter. The result was not satisfactory. Many of the measurements were found to be uncertain and as a result of his study Knibbs doubted whether it was yet possible to determine the viscosity of a substance like water with an error of much less than 1 per cent from 0 to 50°, or 5 per cent from 50 to 100°. During the last 20 years investigations have been carried out, which give thoroughly satisfactory and concordant results, as is shown by Table II in Appendix D. The improvement is due to a happier disposition of apparatus for controlling the different correction factors.

Among gases air may be regarded as the standard substance as water is among liquids. And if we compare the numerous values for the viscosity of air obtained prior to 20 years ago, the result is discouraging and has been often commented upon. These values are given for 0° in Table XX.

TABLE XX.—VISCOSITY OF AIR AT 0°C.

Method	φ	φ	Observer
Transpiration..........	5,942	.....	Graham (1846)
Oscillating disks.......	.....	5,325	Maxwell (1866)
Oscillating disks.......	.....	5,814	Meyer and Springmühl (1873)
Oscillating disks.......	.....	5,590	Puluj (1874)
Oscillating disks.......	.....	5,556	Puluj (1874)
Transpiration..........	5,854	.....	Obermayer (1875)
Oscillating disks.......	.....	5,489	Puluj (1876)
Transpiration..........	5,951	.....	Obermayer (1876)
Transpiration..........	5,650	.....	E. Wiedemann (1876)
Transpiration..........	5,988	.....	Obermayer (1876)
Transpiration..........	5,952	.....	Obermayer (1876)
Transpiration..........	5,848	.....	O. Meyer (1877)
Transpiration..........	5,882	.....	O. Meyer (1877)
Transpiration..........	5,747	.....	O. Meyer (1877)
Oscillating disk........	.....	5,714	Puluj (1878)
Transpiration..........	5,650	.....	Hoffman (1884)
Oscillating disk........	.....	5,955	Schumann (1884)
Oscillating disk........	.....	5,838	Schneebeli (1885)
Oscillating cylinder....	.....	5,831	Tomlinson (1886)
Transpiration..........	5,770	.....	Breitenbach (1899)
Oscillating cylinder....	.....	5,659	F. Reynolds (1904)
Transpiration..........	5,761	.....	Tänzler (1906)

The transpiration method appears to give higher values for the fluidity than are obtained by the other methods but the results are not very consistent among themselves. However the following table of recent values for the viscosity of air at 15° is very satisfactory.

We have the authority of Fisher (1909) page 150, for the statement that "No experimenter has made the attempt to apply a correction to his measured pressures to allow for the kinetic energy of the emerging gas." It appears probable that the exist-

TABLE XXI.—VISCOSITY OF AIR AT 15°

Method	φ	Observer
Transpiration.................	5,507	Breitenbach (1899)
Transpiration.................	5,502	Schultze (1901)
Transpiration.................	5,528	Markowski (1904)
Transpiration.................	5,502	Schmitt (1909)
Transpiration.................	5,531	Knudsen (1909)

ing data might be improved by a critical study for the purpose of making the needed corrections. It is a curious fact that the kinetic energy correction has been so little understood and appreciated. Even in the case of liquids it is very commonly neglected although it may amount to several per cent of the viscosity to be measured. It is sometimes stated that no kinetic energy correction is necessary when liquids flow through a capillary from one reservoir to another and not into the air. The Ostwald viscometer (*cf.* p. 75), is used more than any other but it appears that no kinetic energy correction is ever applied. It is true that the instrument is used for relative measurements only, but this fact does not cause this correction to be without effect in the calculation, for the reason that the kinetic energy correction is not proportional to the viscosity.

There may be those who would maintain that the correction for kinetic energy, as given above, is not the correct one to apply to gases, *cf.* Fisher (1909). But that a correction is unnecessary cannot be maintained even in the case of gases, in view of Hoffmann's work on the interrupted flow of gases. One of his capillaries was cut into 28 pieces without loss. In flowing through the interrupted capillary, the kinetic energy correction would be increased twenty-eight fold, as has been already indicated on page 28. As a matter of fact the time of flow was considerably greater in the interrupted capillary, proving the importance of the correction. It would be particularly interesting to see whether an experimental verification of the correction would be obtained by an intensive study of the data of Hoffmann (1884).

The term "specific viscosity" has been very largely used and may here receive brief comment. Water at 0° has been taken as a standard with a specific viscosity of 100, but water at 25°

has also been taken as the standard and equal to unity. Still other standards have been employed. The principal advantages in this form of expression are the saving of labor in calculation, the avoidance of inconveniently small fractions, and the use of a common liquid as standard. This advantage however is more than offset by the disadvantages. The proper corrections are never applied to specific viscosities and consequently the values are not really comparable among themselves. Certainly they are inconvenient to use for reference and for comparison with viscosities calculated in other ways. The time necessary for the preparation of the substances is nearly always great enough to justify the inconsiderable expenditure of time necessary for the proper reduction of the data to absolute units.

Of course much depends upon the disposition of the apparatus used in the measurement. Some forms of apparatus will not permit accurate estimations of the viscosity to be made. But given an apparatus which is well-suited for precise measurements, the time required for making a measurement is no greater, and may be much less, than in the less accurate forms of apparatus.

The Centipoise.—In expressing viscosities, it is possible to secure simultaneously the advantage of expression in absolute units with the advantages of viscosities relative to some common substance as standard. It is proposed to name the absolute unit of viscosity after Poiseuille the "poise," and consequently the submultiple of this unit which is one-hundredth as large the "centipoise" (*cp*). It so happens that one centipoise is almost exactly the viscosity of water at 20°C, hence absolute viscosities expressed in centiposes are also specific viscosities referred to water 20°C as standard. To be sure the viscosity of water is not exactly one centipoise at 20°C but it is 1.005 which is unity within the limits of possible experimental error in ordinary measurement (*cf*. Appendix D, Table II).

All fluidities are expressed in absolute units, water at 20° having of course a fluidity of 100 units.

CHAPTER V

THE VISCOMETER

A very full discussion has been given of the theory of the transpiration method. Much matter of great historical interest in regard to the various other methods has been passed over. This has been done in order to present the matter which will be of greatest use to the worker. At present the transpiration method is by all odds the most important, this superiority being based upon the following advantages: (1) It is susceptible of simple mathematical treatment. (2) It is rapid. (3) Only a small amount of fluid is required. (4) It can be used under the widest variety of conditions as regards temperature, pressure *et cetera*. (5) The preliminary measurements and adjustments are not difficult to make. (6) Finally, it has been tested out most thoroughly and found to be capable of the highest degree of precision.

For certain purposes other methods must apparently continue to be used. Thus the pendulum method seems best suited for investigating superficial viscosity and the viscosity of solids like steel. The fall method is of great use also for certain purposes.

It is quite impracticable to discuss here the almost innumerable forms of instruments which have been suggested for use, so we propose to consider briefly some of the instruments which have shown the greatest advance toward meeting the conditions of an ideal disposition of apparatus.

Naturally all transpiration instruments are based upon that of Poiseuille; but for general purposes, his instrument was deficient, since the capillary terminated directly into the bath and hence the apparatus had to be refilled after each measurement. This difficulty was overcome in two forms of apparatus designed by Přibram and Handl (1880), which consisted of a capillary placed between two tubes of larger bore. In the better form shown in Fig. 20, the two tubes are vertical, the capillary being bent. The advantage of this arrangement is immediately apparent

because as soon as a measurement has been made in one direction, the apparatus is ready for an observation in the opposite direction. With this apparatus Pribram and Handl made very numerous observations on organic liquids over a range of temperature. They used a constant pressure head.

The apparatus of Brückner (1891) marked another step in advance. He used a horizontal capillary *K*, Fig. 21, connected to the two limbs of the apparatus by means of short pieces of rubber tubing. Two reservoirs *R* and *R'* served for the deposition of any dust particles that might have found their way into the liquid. The volumes of flow were accurately measured by the volumes of the bulbs *V* and *V'*, the tubes leading from ·these bulbs being constricted
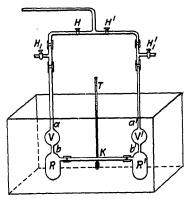
Fig. 20.—Viscometer of Pribram and Handl.

Fig. 21.—Viscometer of Brückner.

in order to give a sharp reading. Either limb could be turned to pressure at *H* or *H'*, or to air at H_1 or H'_1.

In the study of organic liquids rubber connections become objectionable, hence Thorpe and Rodger (1894) in their monumental work on the relation between the viscosity of liquids and their chemical nature, employed an instrument, Fig. 22, similar to that of Brückner except that the capillary was placed inside of a wider tube which was itself subsequently sealed to the two limbs of the viscometer. The middle of this tube was heated at

its middle point until it attached itself to the capillary all of the way around, the greatest care being taken not to decrease the diameter of the capillary or change it in any way.

Another marked improvement was the introduction of the traps T^1 and T^2, Fig. 22, for the purpose of easily adjusting the total volume of liquid within the instrument, which they denoted as the "working volume" to distinguish it from the volume of efflux V. By keeping the working volume constant, the correction for the hydrostatic pressure within the instrument is greatly simplified.

Unfortunately Thorpe and Rodger's instrument has not come into general use. This is probably due to the following disadvantages: The sealing of the wide tube to the middle of the capillary is difficult to accomplish; and according to Knibbs (1895) and Blanchard (1913) one cannot be sure that the bore of the capillary has not been altered in spite of the utmost precaution. It is practicable to get the dimensions of the capillary and the other constants of the instrument only after the sealing has been completed. To get them then is a matter of some difficulty if not uncertainty. The instrument is difficult to clean and dry on account of the narrow spaces between the capillary and the wider tube at either side of the constriction R. At the same time the instrument is rather fragile. These difficulties may all be overcome by using ground glass joints between the capillary and the two limbs. Over the ground-glass joints rubber tubing may be stretched and tied and thus any danger of a leak guarded against. The absence of a leak can be proven very easily at any time by simply testing the working volume. By having good ground-glass joints there can be no change in volume due to the change in the expansion of the rubber under the changing head and there can be no solvent action except that on the glass itself. On the other hand, by planing the ends of the capillary off at

FIG. 22.—Viscometer of Thorpe and Rodger.

right angles to the axis of the tube, the dimensions of the capillary may be most accurately ascertained. There is the further advantage that other capillaries may be used without changing the other constants of the apparatus. It is perhaps unnecessary to add that this instrument must be modified to make it suitable for the measurement of gases.

The Most Suitable Dimensions for a Viscometer.—As we shall see in Part II, it is more convenient to compare fluidities than viscosities. Combining Eqs. (8) and (12) we obtain for the general formula for the fluidity of all fluids

$$\varphi_t = \frac{8\pi Vlt}{\pi^2 gpl^2(R^4 + 4\lambda R^3) - m\rho V^2},$$ (20)

where R is the radius and l the length of the capillary in centimeters, and V is the volume in cubic centimeters, all being reduced to the same temperature. No correction is necessary for changes in these dimensions later since the changes just neutralize each other as can be proved by introducing the coefficient of expansion into the above formula. The pressure p, expressed in grams per square centimeter, is the difference between the absolute pressures at the level of the capillary at the entrance, P_1 and exit, P_2. The time of flow in seconds is t, for the fluid whose density is ρ at the temperature of observation T. $\pi = 3.1416$, g is the acceleration due to gravitation, $m = 1.12$, λ is the coefficient of slipping, which is negligible for all liquids but is of importance in rarefied gases, *cf.* page 244. In the measurement of the fluidity of gases the volume of efflux must be calculated according to the formula of page 50.

$$V = \frac{2P_1}{P_1 + P_2}V_1 = \frac{2P_2}{P_1 + P_2}V_2,$$

where V_1 is the volume of flow as measured before flow under pressure P_1 and V_2 is the volume after expansion to the pressure P_2.

By the proper choice of the dimensions of the apparatus an accuracy of one-tenth of 1 per cent may probably be attained. With a stop-watch reading to 0.2 sec. the time of flow may be made as small as 200 sec. The volume of flow should be small for the following reasons. (1) The kinetic energy correction $m\rho V^2$ in Eq. (20) should be kept from becoming inconveniently

large.   (2) The time of flow should be small for the sake of economy and also that the temperature may be more readily kept constant during the time of flow.   (3) Small masses of fluid come to the temperature of the bath more quickly, and (4) there is an economy in material, which is sometimes very important. The minimum of flow is determined by our ability to read the volume with the desired accuracy.   This in turn is determined by the diameter of the constricted portions of the instrument above and below the measured volume V.   If, however, the constricted parts are of very small bore, the capillary action becomes disturbing.   Very viscous liquids will not drain out properly and they may even form a meniscus across the capillary which will prevent the transmission of the pressure and will render the results quite valueless.   It may be remarked that the troubles due to bad drainage may be minimized by having the drainage surfaces everywhere as nearly vertical as possible.   In other words, the change from constricted portion to the tube of large diameter should be made gradually.   If the constricted part of the instrument has an inside diameter of 0.25 cm we believe that the capillary correction will not cause trouble.   The volume per centimeter of the constricted tube is then 0.05 ml and if we assume that the meniscus can be read to 0.01 cm as it passes a mark on the tube, it is only necessary to have a volume of 0.5 ml to obtain the desired accuracy.   To provide a margin of safety in the construction and use of the apparatus we select about 3 ml as the minimum.

To detect any error due to faulty drainage, it is only necessary to test the flow of the most viscous liquid to be measured using very different rates of transpiration by varying the pressure. Lack of perfect drainage will be made evident, by the substance appearing to be more viscous at the lower rate of flow.   Naturally the more viscous liquids must be allowed to flow slowly enough so that the drainage will appear to be perfect.   If in the instrument depicted in Fig. 23 the flow were to begin with the upper meniscus at the point marked 3, it would be necessary for all of the liquid of the measured volume V to have drained out at the expiration of the time t.   This is not necessary, however, if the flow begins at some point considerably higher up, as for example in the neighborhood of the trap-opening F, for then a certain
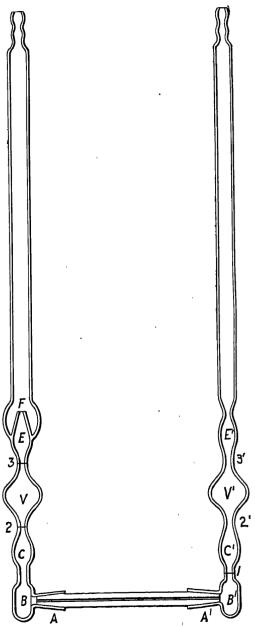
Fɪɢ. 23.—Viscometer for absolute measurements.

amount of liquid may flow into V from E after the record of the
time has begun, and this will tend to offset the effect of any liquid
left in V at the end of the time of flow. To make these amounts
as nearly equal as possible, the lower part of E should be exactly
similar in shape to the lower part of V.

The pressure should be variable at will so that the time of
flow may be kept reasonably constant. For gases, high pressures
are as unnecessary as they are undesirable. For incompressible
fluids, there need be no upper limit set to the pressure. A pres-
sure of 50 g per square centimeter can easily be read to 0.1 per
cent on a water manometer, and the various pressure correc-
tions—to be discussed—may be ascertained well within this
limit, hence this may be taken as a lower limit.

The measurement of the radius of the capillary offers the great-
est difficulty in viscosity measurement by this method. Since
the flow is proportional to the fourth power of the radius, any
error in this measurement is multiplied four times. Careful
weighing of the quantity of mercury required to fill the tube is
perhaps the best means for obtaining the mean radius, $R = \sqrt{(W/\pi\rho l)}$; but for a capillary such as that used by Thorpe and
Rodger, $l = 4.9+$ cm $R = 0.0082+$ cm, the weight of the mer-
cury is only about 0.013 g so that the desired accuracy is diffi-
cult to obtain with the ordinary balance. If the radius is
increased, the time of flow may be kept constant by increasing
the length so that the ratio l/R^4 is constant. Fortunately both
of these changes tend to increase the volume of the capillary.
At the same time the increase in length diminishes the effect
of any possible alteration in the stream lines near the ends; and
the increase in the radius diminishes the possible effect of slip-
ping and probably also the effect of dust particles.

The formula (20) applies only to a capillary which has the
form of a true cylinder, but usually the capillary is elliptical and
it may at the same time be conical. To determine the conicity,
the tube must be calibrated with a mercury thread. To deter-
mine the ratio of the axes, the micrometer microscope should
be used. In using the micrometer microscope it is somewhat
difficult to see the exact circumference to be measured, owing to
various causes. Poiseuille found it best to grind off and polish
the end of the tube and then attach a cover-slip to this end by

means of Canada balsam which is warmed slightly until it fills the end of the capillary.

If the capillary is elliptical, R^4 in Eq. (20) must, according to Rücker (*cf.* Thorpe and Rodger (1893)), be given the value $\dfrac{2B^3C^3}{B^2 + C^2}$ where B and C are the major and minor axes of the elliptical cross-section. If the capillary is the frustrum of a circular cone, Knibbs has shown that R^4 must be replaced by

$$\frac{3R_1^3R_2^3}{R_1^2 + R_1R_2 + R_2^2}$$

where R and R_2 are the radii of the two ends. If the capillary is at the same time elliptical, R^4 becomes

$$\frac{3R_3^3R_4^3}{R_3^2 + R_3R_4 + R_4^2} \cdot \frac{(1 - e^2)^3}{1 + e^2}$$

where R_3 and R_4 represent the arithmetical means of the major and minor radii at their respective ends, and $e = \dfrac{B - C}{B + C}$ where B and C represent the mean semi-axes. Knibbs has also considered the corrections necessary for other peculiarities in the bore of the tube which need not be considered here.

There is no special advantage in using a variety of viscometers for liquids of not very different fluidity. For liquids below the boiling-point the fluidity never exceeds about 500. Assuming this value as the maximum the lengths necessary for a capillary of a given radius have been calculated by means of Eq. (5) and plotted curve A in Fig. 24. It is not always possible to obtain a capillary of an exactly specified radius, but with one having an approximately satisfactory radius, the necessary length can be read off from the curve. For gases the maximum fluidity must be taken as 10,000. If only very viscous liquids are to be measured the maximum may be taken as less than 500, curve B or C. (*cf.* also Appendix A, Table IX.)

Construction and Calibration of Apparatus.—A point of great importance in the construction of the viscometer is to have the volume V (1) as nearly equal to that of V' as possible, (2) similar to it in shape, and (3) at the same height from the horizontal capillary. This construction greatly facilitates the estimation of the correction for hydrostatic pressure, within the

instrument. Finally the small bulbs B, E, B', and E' should have nearly the same volume. By having the surfaces nowhere depart greatly from the vertical, the drainage is improved. It is impracticable however to use long, cylindrical bulbs, since then the true average pressure, due to the hydrostatic head within the instrument, becomes awkward to determine. (*Cf.* Appendix A, page 298.) The best form for the bulbs V and V' is therefore obtained by making them so that each resembles as much as
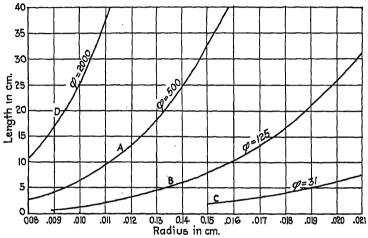
FIG. 24.—Chart for use of instrument maker in selecting capillary for viscometer, knowing the approximate radius of the capillary and the maximum fluidity to be measured, the length to be used may be read off. $V = 3$ml $t = 200$ sec., $p = 50$ g per cm².

possible a pair of hollow cones, placed base to base as shown in Fig. 23.

The marks at l and l' are so placed that the volume from l to F' is exactly equal to that from l' to F. If the two limbs of the apparatus are similar there will be no correction for capillarity. Poiseuille has given a method for estimating this correction when that is necessary. The volumes V and V' may be easily determined by the weight of volumes of mercury.

The appearance of the complete apparatus used by Thorpe and Rodger is shown in Fig. 25. The viscometer is shown in the bath B which has transparent sides. Water in the vessel R exerts pressure upon the air in the large reservoir L. The gas
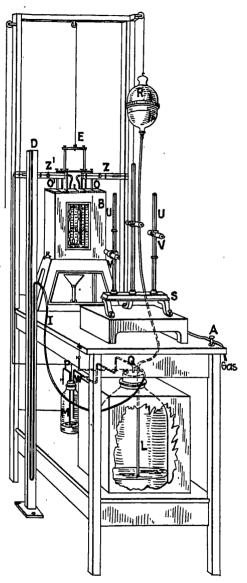
FIG. 25.—Complete viscometer apparatus of Thorpe and Rodger.

is dried, by passing over sulfuric acid in a smaller bottle M, whence tubes lead to the three-way stop cocks Z and Z' and thence to the two limbs of the viscometer. The pressure is measured on the water manometer D. The bath is stirred by means of a motor connected with the mechanism shown at E. Since the fluidity of a substance like water changes from 1 to 3 per cent with a change of $1°$ in the temperature, it is necessary that the temperature be controlled to a few hundredths of a degree. Since they were working over a wide range of temperature, Thorpe and Rodger controlled the temperature by hand.

A word may be added here in regard to stop-watches. The common form of stop-watch in which the whole mechanism starts or stops simultaneously with the time record may not give consistent results, even though it appears to neither gain nor lose during a long period of time. This is the fault of the mechanism. The watches whose movements continue, whether the time is being recorded or not, seem to be freer from this defect.

Fig. 26.—Apparatus of Thorpe and Rodger for obtaining dust-free liquid.
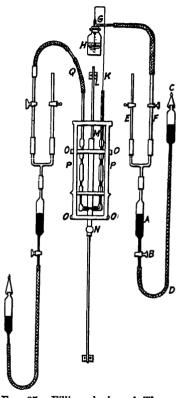
The Measurement.—In preparing substances for measurement as well as in cleaning and drying the instrument, many investigators have strongly emphasized the importance of avoiding the presence of dust particles. Both Poiseuille and Thorpe and Rodger took elaborate precaution in this regard. Figure 26 shows the apparatus used by the latter for distilling pure liquids. It has the advantage of allowing a good determination of the boiling-point to be made while the liquid is being fractionated. To avoid contamination by dust and moisture in filling the viscometer, Thorpe and Rodger used a special apparatus, Fig. 27. The liquid was placed in the bottle H and forced over into the right limb of the viscometer M by means of the pressure of a mercury head A. The viscometer was held in a frame and supported on the vertical rod by means of the setscrew N.

The left limb of the viscometer was evacuated by means of the mercury head Q in order to draw the liquid through the capillary.

Having run in a little more than the required amount of liquid, the viscometer and frame were placed in the bath B of Fig. 25 and the limbs of the viscometer were connected to the pressure outlets on either side. With the temperature maintained constant at the lowest point at which measurements were desired, the cock Z' (or Z) was turned to air and the cock Z (or Z') to pressure. As the liquid rose in the left limb, it finally overran into the trap $T,'$ Fig. 22. At the instant that the meniscus in the right limb reached the point k^2, the cock Z was turned to air. Thus the working volume was adjusted.

Fig. 27.—Filling device of Thorpe and Rodger.

A measurement of the fluidity is made by turning the cock Z' to pressure and immediately reading the pressure on the manometer as well as the temperature of the manometer, while the liquid is flowing out of the bulb V. As the meniscus passes the point m' the time recorded is begun. Keeping the temperature constant the time is taken as the meniscus passes the point m^2. The pressure is then read as before, and before the meniscus reaches the point k' the left limb is again turned to air. The apparatus is then ready for a duplicate observation in the opposite direction.

The Calculation.—The corrections to the time and temperature are not peculiar to viscosity measurements and need no special comment. In obtaining the pressure, several corrections must

be made. (1) The pressure on the manometer must be calculated
to grams per square centimeter from the known height of the
liquid and its specific gravity at the temperature observed. A
correction to the observed height of the liquid is avoided by
having the long limb of the manometer doubly bent at its middle
point so that the upper half is vertical and in the same straight
line with the lower limb of the manometer. The levels on both
limbs may then be read on the same scale, which may con-
veniently consist of a steel tape mounted on a strip of plate-glass
mirror placed vertically. Similarly a correction for capillary
action may be avoided if the bore of the manometer is large
enough so that it may be assumed to be uniform. (2) The pres-
sure must be corrected for the weight of the air displaced by the
liquid in the manometer. (3) Unless the surface of the liquid in
the lower limb of the manometer is at the same height as the
average level of the liquid in the viscometer, a correction must be
made for the greater density of this enclosed air, than of the
outside air which is not under pressure. (4) Finally a correction
must be made for the average resultant hydrostatic head of the
liquid within the viscometer. If the two volumes V and V'
in Fig. 23 are exactly equal in volume, similar in shape, and
at the same elevation above the capillary, when the viscometer is
in position, in the bath, it is evident that the gain in head during
the first half of the flow will be exactly neutralized by the loss
in head during the last half of the flow. Since this cannot be
exactly realized, a correction may be made as follows: Duplicate
observations in reverse directions are made upon a liquid of
known density and viscosity at a constant temperature and
pressure. Let t_1 be the time of flow from left to right and t_2 the
corresponding time from right to left. Let p_0 be the pressure as
corrected, except for the average resultant head of liquid in the
viscometer. Suppose this latter correction to amount to x cm
of the liquid as the liquid flows from left to right. In this case
the total pressure becomes equal to $p_0 + \rho x$ and when the
liquid flows from right to left, it becomes equal to $p_0 - \rho x$.
Since Eq. (8) when used for a given viscometer may be written
in the form

$$\eta = Cpt - C'\rho/t \qquad (22)$$

where C and C' are constants, which can be calculated, we obtain

$$p_0 + \rho x = \frac{\eta + C'\rho/t_1}{Ct_1}$$

$$p_0 - \rho x = \frac{\eta + C'\rho/t_2}{Ct_2}$$

whence,

$$\mathbf{x} = \frac{\eta}{2C\rho}\Big[\frac{1}{t_1} - \frac{1}{t_2}\Big] + \frac{C'}{2C}\Big[\frac{1}{t_1{}^2} - \frac{1}{t_2{}^2}\Big]$$

In subsequent calculations it is necessary to know the specific gravity of the liquid whose viscosity is desired, in order to make the necessary pressure correction and in order to make the kinetic energy correction, but it is to be noted that if the instrument has been constructed with that end in view, these corrections will both be small, and therefore the specific gravity need be only approximately known, which is a great advantage.

Relative Viscosity Measurement.—On account of the labor involved in obtaining the dimensions of the viscometer, many investigators have followed the example of Pribram and Handl in disregarding these dimensions, and calibrating the instrument with some standard liquid. The most important instrument of this class is that of Ostwald, Fig. 28. It consists essentially of a U-tube with a capillary in the middle of one limb above which is placed a bulb. A given volume of liquid is placed in the instrument and the time measured that is required for the meniscus to pass two marks one above and one below the bulb under the influence of the hydrostatic pressure of the liquid only.

FIG. 28.— The Ostwald viscometer.

If η_0 is the viscosity of the standard liquid and η that of liquid to be measured, we have from Eq. (22)

$$\frac{\eta}{\eta_0} = \frac{Cpt - C'\rho/t}{Cp_0t_0 - C'\rho_0/t_0},$$

and if η is very nearly equal to η_0 or if t and t_0 are very large, this may be written

$$\frac{\eta}{\eta_0} = \frac{pt}{p_0t_0}, \tag{23}$$

The pressure in this instrument must be proportional to the densities so that

$$\frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0},$$

which is the formula suggested by Ostwald. The formula is true for dilute solutions when water is taken as the standard, for η is then nearly equal to η_0.

It is inconvenient to make the time of flow very large both on account of the lack of economy and because of the increased danger of clogging. Unfortunately this formula has been used where neither of the necessary conditions was complied with and the results are therefore of uncertain value. It is much better to make the correction for the kinetic energy, in such cases, than to attempt to make the correction negligible.

It is a disadvantage of the Ostwald instrument that the pressure is not variable at will, because if the time of flow is sufficient in one liquid, in another more viscous liquid the time of flow may be intolerably long, practically necessitating the use of a variety of instruments. Furthermore the total pressure is so small that a small error in the working volume may introduce considerable error into the result and the density of the liquid must be known with considerable accuracy.

A form of instrument which has the manifest advantages of the Ostwald instrument and overcomes the above objections is shown in Fig. 29. The volume K is made as nearly as possible equal in volume, similar in shape, and at the same height as C. The working volume is contained between A and H and the volume of flow between B and D, the measurement being made as the meniscus passes either from B to D or from D to B

FIG. 29.—Viscometer suitable for the relative measurement of not too viscous liquids.

depending upon the direction of the flow. The corrections are made as for absolute measurements and the viscosity calculated from formula (22). In obtaining the pressure correction due to the average resultant hydrostatic pressure in the viscometer C' can be estimated accurately enough by means of rough measurements. The value of C can be obtained accurately enough for the calculation of this correction by assuming $p_0 = p$. After obtaining the value of the hydrostatic head x in this way, the true value of C may be calculated from an observation upon the time of flow of any liquid whose viscosity is accurately known. In the use of any relative instrument, it is important that two standards be employed so as to obtain a check upon the method. For this purpose a single liquid may be used at widely different temperatures or two or more liquids may be used of widely different viscosities. While this test is very simple and its importance is obvious, it does not appear to have been frequently employed.

Viscosity Measurements of Liquids above the Boiling-point.— If the viscosity of liquids is to be measured above the ordinary boiling temperature, one must work at pressures above the atmospheric pressure. The three-way cocks in Fig. 22 must lead to a low-pressure reservoir, this pressure being measured by a second manometer. The rubber connections must of course be replaced by others capable of withstanding the desired pressure.

Viscosity Measurement of Very Viscous Substances.—Substances like pitch which are excessively viscous can yet be measured by the efflux method by the use of very great pressure (*cf.* Barus (1893)). On account of the lack of proper drainage,

Fig. 30.—Plastometer. For use with very viscous or with plastic substances.

the apparatus described above is unsuited.   But in this case the
volume may very properly be obtained from the weight of the
efflux into air, because the effect of surface tension would be
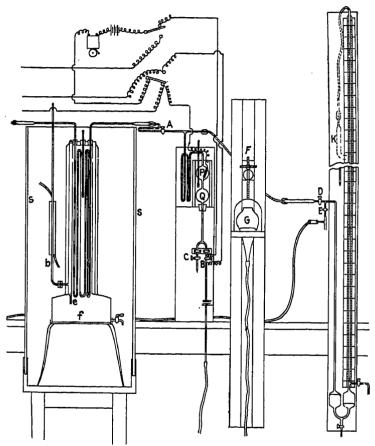
FIG. 31.—Viscometer for gases after Schultze.

negligible at these high pressures.   A viscometer designed for
very viscous substances is shown in Fig. 30.   The use of this
form of apparatus is described in detail in connection with
plastic flow (cf. Appendix B, p. 320).

   The Viscosity Measurement of Gases.—A very satisfactory
apparatus for the measurement of the viscosity of gases by the

efflux method has been worked out through the labors of Graham (1846–1861), O. E. Meyer (1866–1873), Puluj (1876), E. Wiedemann (1876), Breitenbach (1899), and Schultze (1901). We may describe briefly the form used by Schultze as illustrating the modifications which are necessary in the apparatus used for liquids. In Fig. 31 the glass capillary, $l = 52.54$ cm, $R = 0.007572$ cm, is contained in the upper chamber of the bath f, which is maintained at constant temperature by water, water vapor, or aniline vapor. A condenser is shown at b and SS is a shield to protect the rest of the apparatus from the radiation. On either side of the bath the apparatus is exactly similar, so that only the right side is shown in the figure. The gas is contained in the bulbs P and Q (and P' and Q' on the left side) surrounded by a separate bath. The lower bulbs are each connected with two stop cocks B and C (or B' and C'); from B (or B') a rubber tube leads to the mercury reservoir G (or G'), and from C (or C') there is a glass tube drawn out into a capillary. Adjacent to both the capillary and the bulbs, considerable lengths of glass tubing are put in connection and immersed in the respective baths in order that the gas in the capillary or bulbs may be at the desired temperature at the time of measurement. In each tube leading from the bulbs to the capillary there is a stop cock A (and A') and a connection with a manometer K (and K'). By means of stop cocks at E and E' the two manometers may be connected together or gas admitted to the apparatus from outside. Since the presence of water vapor is objectionable and gases are more or less soluble in water, the manometer contains both mercury and water, and is calibrated before use.

In making a measurement, enough gas is admitted into the evacuated apparatus so that at atmospheric pressure, the surface of the mercury is in the lower part of the bulb Q and in the middle part of the bulb Q'. The stop cock A is then closed and the mercury reservoirs G and G' raised, but the former enough higher than the latter so that a pressure head is established which is a few millimeters greater than is desired in the measurement. The mercury fills the two bulbs Q and Q'. When the temperature is constant the stop cock A is opened. The pressure is immediately adjusted and thereafter maintained constant by means of the screws F and F' which serve to slowly

raise or lower the mercury reservoirs. When the mercury passes into the bulb P, contact is formed with a platinum point and an electrical signal given. At this moment the chronometer is started. After the elapse of sufficient time, the stop cock B is closed and thus the current is broken between the two platinum electrodes at either side of this stop cock, and a signal is given. The mercury is now allowed to run out through the stop cock C until the signal is given when the mercury loses connection with the platinum point in the bulb P. From the weight of this mercury, the volume of flow is calculated.

PART II
FLUIDITY AND OTHER PHYSICAL AND CHEMICAL PROPERTIES

CHAPTER I

VISCOSITY AND FLUIDITY

It has been tacitly-assumed by the great majority of workers that when two liquids are mixed, the viscosity of the mixture is normally a linear function of the composition. This appeared as early as 1876 in the work of Wijkander. In a great many mixtures, including practically all of those in which water is a component, the viscosity is certainly very far from being a linear function of the composition, there being often a maximum in the viscosity curves. However water mixtures should not be considered as "normal," but since it is difficult to decide what shall be considered normal mixtures, the question whether the viscosities are additive or not is admittedly difficult of solution. Dunstan (1905) classifies as normal those mixtures whose viscosity-weight concentration curves do not show a maximum or a minimum. This classification is not satisfactory not only because it lacks a theoretical justification but also because many of the so-defined normal mixtures give curves which depart considerably from the linear, so that the suspicion is aroused that the occurrence of a maximum or minimum may depend upon accidental circumstances such as the nearness to equality of the viscosity of the components. The accidental character of such a classification is very striking in mixtures which fall into the normal class at one temperature but at a slightly different temperature must be classified as abnormal.

Such light as can be gained from a study of the viscosities of mixtures, seems to lead to the conclusion that viscosities are not additive, as has been assumed. Thus Dunstan (1904) remarks, "The law of mixtures is never accurately obeyed and

divergences from it seem to be more clearly marked out in the case of viscosity than with other properties, such as refractive index." Thorpe and Rodger (1897) say, "The observations described in this paper afford additional evidence of the fact indicated by Wijkander and supported by Linebarger, that the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the composition. It seldom happens that the liquid in a mixture preserves the particular viscosity it posesses in the unmixed condition. To judge from the instances heretofore studied, the viscosity of the mixture is, as a rule, uniformly lower than the mixture law would indicate, but no simple relation can yet be traced between the viscosity of a mixture and that of its constituents." Thorpe and Rodger were so struck by the absence of linearity in the viscosity curves, that they thought that an explanation was needed for the fact that the viscosity curves of some mixtures measured by Linebarger (1896) are indeed linear. " The observed viscosities in general are less than those calculated by the mixture rule, except, possibly, in the case of mixtures of benzene and chloroform and mixtures of carbon disulfide with benzene, toluene, ether, and acetic ether, where, possibly, the temperature of observation (25°) was too near the boiling-point of the carbon disulfide to make any specific influence, which that liquid might exert at lower temperatures, perceptible."

Lees (1900) showed what are the necessary assumptions in regard to the nature of flow in mixtures, so that the viscosities should be additive, but by making a careful study of existing data, he found little justification for these assumptions. Similarly Lees tried the assumptions that fluidities or logarithmic viscosities are the characteristic additive property, but he was unable to obtain a satisfactory verification of either from the experimental results.

The question before us seems to be: "Is viscosity or fluidity or some function of one of them the characteristic additive property?" The answer to this question is imperative before we can intelligently discuss the relation of viscosity to other properties. This statement requires no proof in view of the statements which we have quoted to show that in some cases the viscosity concentration curve is linear according to assumption, but in the

great majority of cases it is sagged and there is no known law to account for the peculiarity. Surely any discussion of chemical combination or of dissociation on the basis of deviation from the "normal" curve under such conditions would be of very uncertain value.

There are numerous reciprocal relations besides viscosity and fluidity, such as electrical resistance and conductance, or specific heat and heat capacity, or specific gravity and specific volume. It has been repeatedly pointed out[1] that if one of these is additive, its reciprocal cannot be. It is singular enough that among all of these reciprocal relations, viscosity is the only one for which the decision has not been reached as to whether viscosity is additive or not, or if it is, under what conditions. In electricity for example we have absolutely no doubt but that resistances are additive under certain conditions, *viz.*, when the conductors are in series, and likewise that conductances are additive under other equally definite conditions, *viz.*, when the conductors are in parallel. It seems probable that the present unsatisfactory condition as regards viscosity has arisen due to the extraordinary sensitiveness of this property to molecular changes in fluids, either combination or dissociation. We shall attempt to reach a solution of the problem from a consideration of the nature of viscous flow and then test this solution by means of the experimental facts. After we have reached a conclusion in regard to the true additive property under given conditions, it may well turn out that the present unsatisfactory condition will prove to be a blessing in disguise, for it may then be shown that viscosity is of the greatest importance in physiochemical investigations.

The fundamental law of viscous flow

$$\frac{dv}{dr} = \frac{F}{\eta}$$

is the analogue of the well-known electrical law of Ohm. In fact Elie in 1882 suggested a modification of the Wheatstone's bridge method for the measurement of viscous resistance.
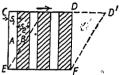
Case I. Viscosities Additive—Emulsions.—We will first consider the very simple case of a series of vertical lamellæ of viscous material arranged alternately, as in Fig. 32, and subjected to a

[1] *Cf.* p. 89.

horizontal shearing stress. For convenience suppose that all of the lamellæ of the one substance A have the same thickness s_1 and that the laminæ of the substance B have the uniform thickness s_2, etc. Let the viscosities of the substances be η_1, η_2 . . . and the shearing stresses per unit area p_1, p_2 . . . respectively; then if R is the distance between the horizontal planes, the velocity of the moving surface is

$$v = \frac{RP}{H} = \frac{Rp_1}{\eta_1} = \frac{Rp_2}{\eta_2},$$

where H is the viscosity of the mixture, and P is the average shearing stress over the entire distance S. But

Fig. 32.—Diagram to illustrate additive viscosities.

$$PS = p_1s_1 + p_2s_2 + \ldots ,$$

hence

$$H = \frac{R}{v}\left(\frac{p_1s_1 + p_2s_2 + \ldots}{S}\right).$$

But since s_1/S is the fraction by volume of the substance A present in the mixture, which we may designate a, and similarly $s_2/S = b$, etc.,

$$H = a\eta_1 + b\eta_2 + \ldots \tag{24}$$

This case is of particular interest in connection with emulsions and many other poorly mixed substances. The formula tells us that the viscosity of the mixture is the sum of the partial viscosities of the components, provided that the drops of the emulsion completely fill the capillary space through which the flow is taking place.

Case II. Fluidities Additive—Fluid Mixtures.—If the lamellæ are arranged parallel to the direction of shear, as shown in Fig. 33, we have a constant shearing stress, so that

$$P = \frac{\eta v_1}{r_1} = \frac{\eta_2 v_2}{r_2} = \ldots \tag{24a}$$

where v_1, v_2, . . . are the partial velocities as indicated in the figure.

There are two different ways of defining the viscosity of a mixture, and it becomes necessary for us to adopt one of these before we proceed further.

1. If we measure viscosity with a viscometer of the Coulomb

or disk type, we actually measure the velocity v, BS in the figure, and we very naturally assume that

$$P = \frac{Hv}{R}$$

2. It is more usual, however, to calculate the viscosity from the volume of flow, as in the Poiseuille type of instrument. Let v', BS' in the figure, be the effective velocity which the surface BS would have, were the series of lamellæ replaced by
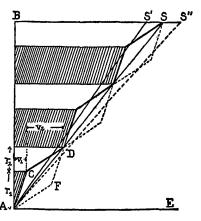
Fig. 33.—Diagram to illustrate additive fluidities.

a homogeneous fluid having the same volume of flow. The effective velocity is related to the quantity of fluid U passing per second in a stream of unit width, as follows:

$$U = \frac{v'R}{2}$$

Let the viscosity as calculated from the flow, as for a homogeneous fluid, be H', then

$$P = \frac{H'v'}{R} = \frac{2H'U}{R^2} \tag{24b}$$

It is to be noted that had the less viscous substance been in contact with the surface AE, the effective velocity of flow would have been represented by the distance BS''. We shall take the former of these for our definition of the viscosity of a mixture,

since, as we shall now show, by using it the viscosity is independent of the number or arrangement of the lamellæ.

Since $v = v_1 + v_2 + \ldots$
we obtain from Eqs. (24a) and (24b) that
$$PR\Phi = P(r_1\varphi_1 + r_2\varphi_2 + \ldots)$$
or since
$$a = \frac{r_1}{R}, \; b = \frac{r_2}{R}, \text{ etc.}$$

the fluidity of the mixture is
$$\Phi = a\varphi_1 + b\varphi_2 + \ldots \tag{25}$$

The fluidities are, according to this definition, strictly additive and entirely independent of the number and arrangement of the layers. Since, however, the viscosities are usually calculated by means of the Poiseuille formula based on the volume of flow, it is important to determine for a given arrangement of lamellæ what correction must be made to the effective viscosity, as calculated from the volume of flow, to make it accord with the true viscosity, as defined above and as obtained by the disk or other similar method for the measurement of viscosity.

Reverting again to the figure, we find that

$$U = \frac{v_1 r_1}{2}$$
$$+ \; v_1 r_2 + \frac{v_2 r_2}{2}$$
$$+ \; v_1 r_1 + v_2 r_1 + \frac{v_1 r_1}{2}$$
$$+ \; v_1 r_2 + v_2 r_2 + v_1 r_2 + \frac{v_2 r_2}{2}$$

If there were n pairs of alternate lamellæ of the two substances A and B

$$U = \frac{1}{2}[n^2 v_1 r_1 + n(n+1)v_1 r_2 + n v_2 r_2 + n(n-1)v_2 r_1] \tag{26}$$

Since $n = \frac{R}{r_1 + r_2}$, on substituting into Eq. (26) the values of v_1 and v_2, we get

$$U = \frac{R^2 P}{2}\Big[a\varphi_1 + b\varphi_2 + \frac{ab}{n}(\varphi_1 - \varphi_2)\Big]$$

and if $\Phi' = \frac{1}{H}$, we obtain from Eq. (24b)

$$\Phi^1 = a\varphi_1 + b\varphi_2 + \frac{ab}{n}(\varphi_1 - \varphi_2) \tag{27}$$

and when $n = \infty$, the fluidity becomes simply

$$a\varphi_1 + b\varphi_2$$

and in this case

$$\Phi' = \Phi. \tag{28}$$

In a homogeneous mixture it appears, therefore, that the two definitions lead to the same fluidity, and experimental results lead us to believe that this is the case usually presented in liquid mixtures, since the disk method and the capillary tube method give the same fluidity so far as we have certain knowledge. If, however, the number of lamellæ is small, which may well be the case in very imperfect mixtures, or when the flow takes place through very narrow passages, the effective fluidity as calculated from the volume of flow may be either greater or less than the sum of the partial fluidities of the components, depending upon the order of the arrangement of the lamellæ in reference to the stationary surface. The amount to be added or subtracted from the effective fluidity in order to obtain the true fluidity is represented by the term, corresponding to the areas ACD, etc. or AFD, etc., Fig. 33.
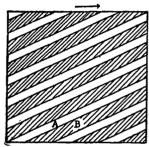
Fig. 34.—Diagram to illustrate how, in incompletely mixed but miscible fluids, flow necessarily brings about complete mixing, so that even when the viscosities were originally additive the fluidities finally become additive. In immiscible fluids, the layers A and B resist indefinite extension and emulsions are the result.

A combination of the cases I and II would lead to a checkerboard arrangement, but it may be shown now that such an arrangement tends to reduce itself to the case II where fluidities are additive.

If the arrangement considered in Fig. 32 is subjected to continued shearing stress, the lamellæ will tend to become indefinitely elongated as indicated in Fig. 34; and unless the surface tension intervenes, as may be the case in immiscible liquids, the lamellæ will approach more and more nearly the horizontal position. Thus, so far as we can determine without going into the complicated problem of the molecular motions, it seems certain that the fluidities will become more and more

nearly additive as the flow progresses and the mixture becomes more and more nearly complete. This result takes place furthermore irrespective of the original arrangement of the parts of the mixture.

Some one may object that a perfectly homogeneous mixture —in itself a contradiction of terms—is not made up of layers such as we have considered in these greatly simplified cases. There can be no doubt whatever of the existence of layers during the process of mixing. No one has watched the drifting of tobacco smoke in his study without noting how it is drawn out into gossamer-like layers.[1] Since the fluidity is least when fluidities are additive, there would have to be a sudden drop in fluidity as the mixture became perfect, if the fluidities were no longer additive. This is not supported by any experimental evidence.

We have already noted that when there is no chemical action between the components of a mixture, the viscosity-concentration curves are usually but not always sagged. Dunstan (1913) has put it: "It can therefore safely be predicted that wherever the two components show little tendency for chemical union a sagged curve, or one departing but slightly from linearity, will be found." If the fluidities of such mixtures are additive, these facts ought to be accounted for by the theory, peculiar as they may seem to be. We shall first prove that according to the theory that fluidities are additive, we should expect the viscosity-concentration curves to be sagged.

Equations (25) and (24) represent the two assumptions that fluidities are additive and that viscosities are additive respectively but for convenience we shall assume that only two components are present in the mixture. From Eq. (23) we get that

$$\frac{1}{\varphi'} = \frac{a}{\varphi_1} + \frac{b}{\varphi_2}$$

or

$$\varphi' = \frac{\varphi_1 \varphi_2}{b\varphi_1 + a\varphi_2}.$$

When $a = 0$ or 1, and $b = 1$ or 0 respectively, φ must be equal to φ'. For all intermediate values of a and b we desire to learn

whether φ must be invariably greater than, equal to, or less then φ'. Multiplying Eq. (25) by unity, we obtain

$$\varphi = \frac{(a\varphi_1 + b\varphi_2)\ (b\varphi_1 + a\varphi_2)}{b\varphi_1 + a\varphi_2}$$

$$= \frac{(a^2 + b^2)\varphi_1\varphi_2 + ab(\varphi_1{}^2 + \varphi_2{}^2)}{b\varphi_1 + a\varphi_2} \gtreqless \frac{\varphi_1\varphi_2}{b\varphi_1 + a\varphi_2} = \varphi'.$$

Since $b = 1 - a$,

$$2a(a - 1)\varphi_1\varphi_2 + a(1 - a)\ (\varphi_1{}^2 + \varphi_2{}^2) \gtreqless 0$$

Discarding the known roots, $a = 0$ and $a = 1$, we get

$$\varphi_1{}^2 - 2\varphi_1\varphi_2 + \varphi_2{}^2 \gtreqless 0,$$

which is a perfect square and therefore must be positive. Hence, when φ_1 is equal to φ_2, φ is equal to φ', but for all other values φ must be greater than φ'. Our conclusions may be stated as follows:

1. The viscosity of a thorough mixture of chemically indifferent fluids must always be less than would be expected on the assumption that viscosities are additive, but this inequality will approach zero as the difference between the viscosities of the components approaches zero.

2. So, on the other hand, the viscosity of an emulsion must be greater than that of a perfect mixture of the same composition, because in emulsions the viscosities tend to become additive.

Equation (25) may be expressed in the form

$$\varphi = \varphi_1 + (\varphi_2 - \varphi_1)b, \tag{29}$$

where φ_1 and φ_2 are constant and φ and b are variable. The corresponding viscosity equation is

$$\eta = \frac{1}{\varphi_1 + (\varphi_2 - \varphi_1)b} \tag{30}$$

It is important to note that Eq. (29) is the equation of a straight line, but that Eq. (30) is the equation of a hyperbola. If we replace $\varphi_1 + (\varphi_2 - \varphi_1)b_2$ by $(\varphi_2 - \varphi_1)m$, where

$$m = a_1 + \frac{\varphi_1}{\varphi_2 - \varphi_1}$$

we get

$$m\eta = \frac{1}{\varphi_2 - \varphi_1}$$

which is the equation of an equilateral hyperbola, whose X-axis is

at a distance $\varphi_1/(\varphi_2 - \varphi_1)$ to the left of the origin to which Eq. (27) is referred.

3. We conclude therefore that the curve obtained by plotting viscosities against volume concentrations is not normally linear but a part of an equilateral hyperbola.

From Eq. (30) we find the curvature for any mixture to be

$$k = \frac{2(\varphi_2 - \varphi_1)^2 [\varphi_1 + (\varphi_2 - \varphi a_1)_1]^3}{\{[\varphi_1 + (\varphi_2 - \varphi_1)a]^4 + (\varphi_2 - \varphi_1)^2\}^{3/2}} \tag{31}$$

By differentiating this curvature in respect to the concentration a and equating to zero, we find the concentration where the curvature is a maximum to be

$$a = \frac{\sqrt{\varphi_2 - \varphi_1} - \varphi_1}{\varphi_2 - \varphi_1} \tag{32}$$

Substituting this value in Eq. (31), the amount of the curvature where the curvature is a maximum, is found to be
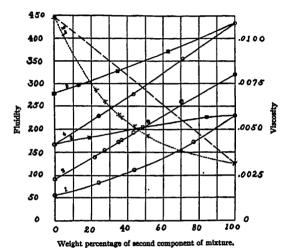
$$k = \frac{\sqrt{\varphi_2 - \varphi_1}}{2}. \tag{33}$$

4. The curvature of the viscosity-volume concentration curves is greatest when the difference between the fluidities, *i.e.*, $\varphi_2 - \varphi_1$, is large, and becomes zero when $\varphi_2 - \varphi_1 = 0$.

5. The curvature must continually decrease as the concentration increases unless the square root of $\varphi_2 - \varphi_1$ is greater than φ_1, in which case the point of greatest curvature will be found at some positive concentration (*cf.* Eq. (32)).

6. Mathematically considered, the curvature is dependent only upon the difference in the fluidities of the components, *i.e.*, $\varphi_2 - \varphi_1$ and not upon φ_1, but since we can only realize positive values of a_1, it follows that for a given value of $\varphi_2 - \varphi_1$ the curvature at any concentration will be greatest when φ_1 is very small.

Liquid Mixtures

The first conclusion is confirmed by the repeated observation that viscosity-concentration curves of homogeneous mixtures are normally sagged. The fourth conclusion offers an explanation of the fact that they are sometimes very nearly linear. In particular, this conclusion is confirmed by Thorpe and Rodger, who, in commenting on the data of Linebarger, make the interest-

ing observation "As a rule, the greater the difference between the viscosities of the pure liquids, the greater is the difference between the calculated and the observed values of the mixtures." The second conclusion is confirmed by the sudden drop in the fluidity of a mixture as it is cooled below its critical-solution temperature. This has often been noted and commented upon, and will be discussed more fully at a later point. In undercooled liquids

FIG. 35.—1. Fluidity curve of nitrobenzene and ethyl acetate at 25°; 2. Fluidity curve of ethyl alcohol and acetone at 25°; 3. Fluidity curve of benzene and ethyl acetate at 25°; 4. Fluidity curve of benzene and ethyl ether at 25°; 5. Fluidity curve of carbon bisulphide and ethyl ether at 25°; 2η. Viscosity curve (dotted) of ethyl alcohol and acetone at 25°. Were viscosities additive, this curve would be linear (dashes).

and other very viscous substances it has been often noted that the viscosity curves have a very high degree of curvature, at least during a part of their course. This is in harmony with the fifth and sixth conclusions.

Were the fluidity-volume concentration curves invariably linear, it would constitute an experimental verification of our fourth conclusion. Unfortunately for this purpose, the fluidity concentration curves are rarely, if ever, perfectly linear, for the reason that has been indicated; *viz.* that there is perhaps nearly always some molecular change on mixing, even though very feeble, and to this change fluidity is very sensitive. These

changes are of no interest to us at this point, but the fact is very important for us that the fluidity-volume concentration curves are much more nearly linear than the viscosity concentration curves. To become convinced of this the reader should plot the fluidity concentration curves of several of the mixtures given by Wijkander (1878), Linebarger (1896), Dunstan *et cet.* (1904) and others and compare them with the viscosity curves given by those authors. A few of these curves are given in Fig. 35.[1] Kendall (1913) has gone over the whole range of available data and finds that the percentage deviation between the observed and calculated values is 11.1 for the viscosity curves and 3.4 for the fluidity curves.

Fluidity and Temperature

The conclusion that fluidities are additive has far-reaching consequences, so that there arise tests for the conclusion which were at first quite unsuspected. For example, it is evident that the reasoning which has been found to hold for mixtures of fluids must also hold for mixtures of the same fluid at different temperatures; for a fluid at any temperature may be thought of as a mixture of appropriate amounts of portions of the fluid maintained at the extreme temperatures. Hence, we are led to the hypothesis that the fluidity-temperature curves of pure fluids should normally be linear, and the viscosity-temperature curves hyperbolic. This relation cannot hold through a change of state because a new cause of viscosity then enters in. Furthermore the fluidity of liquids is closely related to their volumes, as we shall see later, and the volumes of liquids do not generally increase in a linear manner with the temperature. Then, too, association and dissociation may play a disturbing factor, so that as in mixtures, a perfect verification can scarcely be expected. In Fig. 36 there are given the fluidity-temperature and viscosity-temperature curves of mercury and of water from 0 to 100°C. Both of the

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[1] We have here but a rough test of the truth of the hypothesis that fluidites are additive in homogeneous mixtures, because the fluidites of the components are too close together, all of the components are certainly not inert, and volume concentrations should have been studied. More rigorous tests of the hypothesis will be made after the law of Batschinski has been considered.

fluidity curves are much more nearly linear than are the viscosity curves, the true linear curve being represented in each case by a series of dashes. Mercury is an ideal substance in this connection for it is far removed from the critical temperature, it is not highly associated, and its volume increases in a linear manner with the temperature.[1] The fluidity curve is almost perfectly linear, what curvature there is being in a direction opposite to that of every other known substance, so that it can hardly be
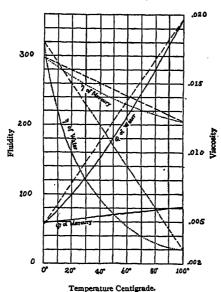
Fig. 36.—Fluidity (continuous) and viscosity (dotted) temperature curves for mercury and water.

regarded as certain that this deviation is not due to experimental error. An extensive study of the fluidity-temperature curves of pure liquids leads to the conclusion that even when the expansion is not linear and there is association, the curves approach linearity, as is seen to be the case with water in the figure. The extent to which this is true can be best judged by an algebraic analysis of the data to be given later. However it may be stated here that the first approximation of Meyer and Rosencranz (1877)

$$\eta = \frac{c}{1 + aT} \tag{34}$$

[1] Landolt and Börnstein, Tabellen, 3d. ed., p. 41.

when put in the form

$$\varphi = A + BT \qquad (35)$$

is but an algebraic expression of the law that the fluidity of a
liquid is a linear function of the temperature. The law is only
approximately true, but even with the alcohols where the curva-
ture is greatest, there is an approach to linearity at high tempera-
tures. Like the Law of Boyle, we may assume that this law holds
in ideal cases, and that the theory underlying it is valid.

EMULSIONS

The study of the viscosity of mixtures near their critical-
solution temperatures affords another very sharp and distinct
means for testing the theory which has been outlined. It has
been pointed out that the fluidities should be additive in the per-
fect mixture but the viscosities additive in the emulsion.
According to the second conclusion page, 89, there should be a
sudden drop in the fluidity at or near the critical solution tempera-
ture. We do not propose to discuss in detail here the viscosity
of colloids but it is appropriate here to seek an answer to the ques-
tion "Has such a drop in fluidity ever been observed?"

Ostwald and Stebutt (1897) observed an abnormally large vis-
cosity mixture of isobutyric acid and water in the neighborhood
of the critical-solution temperature. This was attributed by
them—not to the reason given above—but to the fact that at the
critical-solution temperature, the surface energy becomes zero.

Friedländer (1901) investigated the phenomena which are
peculiar to the critical-solution temperature in an intensive
manner. He found a very marked increase in the viscosity as
the solution was cooled to temperatures where the opalescence
became evident and the critical-solution temperature was
approached. He observed the opalescence with particular care.
His investigation was extended to include phenol and water,
and the ternary mixture of benzene, acetic acid, and water.
Similar relations were found in all proving that the phenomena
are quite general. He concluded that the temperature coefficient
of viscosity is greatest where the opalescence and the tendency
to foam are greatest. He says,[1] "Der Trübungsgrad und Tem-
peraturkoefficient der inneren Reibung zeigen eine starke Zu-

[1] Friedländler, 439.

nahme im kritischen Gebiete und stehen mit einander in einem innigen Zusammenhange." Friedländer also observed that the expansion coefficient and the coefficient of electrical conductivity as well as the refractive index remained normal. He believed that it was necessary to go farther than had Ostwald and Stebutt in order to reach an explanation, and that a definite radius of curvature of the separating surfaces must correspond to each temperature, otherwise the degree of opalescence could not be definitely determined. He therefore attributed the increase in viscosity to the formation of drops, but he was puzzled by the fact that when a solution of colophonium in alcohol is poured into a large quantity of water, a highly opalescent liquid is obtained which has, nevertheless, practically the same viscosity as pure water. This theory of Friedländer is apparently an outgrowth of the theory of "halbbegrenzte Tropfen" of Lehmann. Friedländer also discussed the electrical theory of Hardy that an increase of work would be required to move the particles of a liquid among charged particles, so that if the "drops" were charged an increase in viscosity might result. But by experiment Friedländer found that an electrical field was without noticeable effect upon an opalescent liquid.

Friedländer's values are expressed in relative units. Scarpa (1903) and (1904) has measured the viscosity of solutions of phenol and water, expressing his results in absolute units. For a given temperature, he plotted the viscosities against the varying concentrations, and obtained a point of inflection in the curves at the critical-solution temperature. He tried to explain the irregularities on the assumption that hydrates are formed. He was apparently unfamiliar with the work of Friedländer.

Rothmund (1908) started from Friedländer's work to make a study of the opalescence at the critical temperature. He measured the times of flow of butyric and isobutyric acid solutions in water, noting particularly the effect upon the opalescence of adding various substances, both electrolytes and non-electrolytes. He objected to the hypothesis of Friedländer in that, according to the well-known formula of Lord Kelvin, small drops are less stable than large ones, so that the former must tend to disappear. Furthermore he remarked upon the entirely analogous opalescence which is observed in a single pure substance at its ordinary

critical temperature. Rothmund therefore called to his aid Donnan's hypothesis that when drops are very small their surface tension is very different from that of the liquid in bulk and is a function of the radius of curvature. Since at the critical temperature the surface tension is normally zero, it was thought that the small drops might thus exist in a state of stable equilibrium in the neighborhood of the critical-solution temperature. As the temperature is raised the opalescence would become less and less, due to the solution of the drops. Rothmund found that the addition of naphthalene to his solutions greatly increased the opalescence, while the addition of grape sugar decreased it very greatly, although the effect of these additions upon the viscosity was negligible. He reasoned that the refractive index of butyric acid is greater than that of water and sugar and electrolytes raise the refractive index of water, hence they make the presence of small drops less evident. Naphthalene does not dissolve in water but does dissolve in butyric acid, raising its refractive index, and therefore it makes the opalescence more apparent.

Von Smoluchowski (1908) regards Rothmund's hypothesis as superfluous, believing that the kinetic theory is sufficient to explain the opalescence. According to him, differences in molecular motion, local differences in density, and therefore differences in surface tension cause the critical temperature to be not entirely definite. Due to this indefiniteness in the critical temperature, rough surfaces are formed, which must have a thickness of less than a wave length of light, since greater thicknesses would not reflect the light. The inequalities in the density would reach their maximum at the critical temperature.

Bose and his co-workers (1907–1909) have also verified these earlier observations that abnormally large viscosities are obtained at the critical-solution temperature. Bose regards this as due to the rolling of drops of liquid along the capillary. They did a considerable amount of work to prove that "crystallin" or "anistropic" liquids are similar to the emulsions here discussed. Bose proved that these liquids have abnormal viscosities near the clarifying point and they also possess marked opalescence. Vorländer and Gahren had found that a crystallin liquid may result from the mixing of two liquids neither of which is itself "crystallin" in the pure condition. The mixture therefore

resembles an emulsion. Bose regards all "crystallin" liquids as emulsions of very long life, *i.e.*, they settle out with extreme slowness, and he proposes an extension of the kinetic theory to account for them. According to van der Waals, the molecules are to be regarded as spheres; however, the molecules of substances known to form crystallin liquids do not approximate to a spherical form but consist of two benzene rings united in such a way as to make a rather elongated molecule. Hence, Bose thinks that they may be better represented by ellipsoids of revolution. As the temperature is lowered, these molecules naturally arrange themselves with their long axes in parallel planes. As the molecules unite to form the so-called "swarms," the viscosity is increased. This orderly arrangement also causes the liquids to show double refraction.

It was shown that quite often the viscosity *increases* rapidly as the temperature is raised at the clarifying point, but there is also then an increase in the density.

It occurred to Bose, Willers, and Rauert (1909) that the orderly "swarm" arrangement might be destroyed by measuring the viscosity under conditions for turbulent flow. It was shown by them in fact, that the abnormalities at the critical-solution temperature do decrease as the transpiration velocity is increased. But these results are not very conclusive since the measurement of viscosity under conditions for turbulent flow has been but little investigated. Pure liquids were studied by them under conditions for turbulent flow and it was found that there is not a complete parallelism between the viscosities as measured by the two methods. In fact, there are several cases where one substance has a higher viscosity than another substance under conditions for linear flow, but a lower apparent viscosity under conditions for turbulent flow. No explanation seems to have been given for this.

Tsakalotos (1910) has studied mixtures which show a lower critical-solution temperature, triethylamine and water, and nicotine and water, as well as amylen and aniline, and isobutyric acid and water. He used only one or two temperatures so that the peculiarity with which we are here concerned did not appear.

Bingham and White (1911) investigated phenol and water mixtures with the following results. (1) The fluidity decreases

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unusually rapidly as the solutions are cooled toward the critical-solution temperature. (2) But this abnormality appears before the critical-solution is reached and continues on and through the critical-solution temperature. (3) In the region where the abnormality appears, it is very difficult to obtain concordant values for the apparent fluidity. It may be added that this is to be expected since according to the theory, the apparent fluidity depends upon the size of the drops. (4) By reflected light the solutions in this region appear opalescent: by direct light the liquid shows unequal refraction, the images of objects being distorted.

Drapier (1911) studied two mixtures in which water is not a component, *viz.* hexane and nitrobenzene, and cyclohexane and aniline. The fluidity-temperature curves and the fluidity-weight concentration curves of the latter are shown in Fig. 37. Drapier states that the relations are similar when volume-concentrations are employed. According to his experiments, the contention that fluidities are normally additive in homogeneous mixtures is fully sustained.
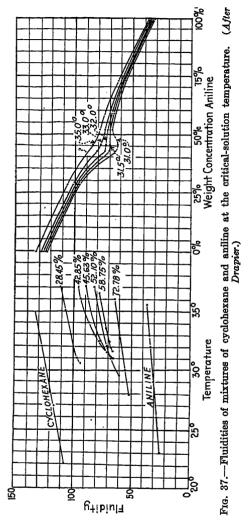
"Il semble donc que dans un intervalle assez étendu de variation de température on puisse considérer la fluidité comme une fonction linéaire de la température, sauf pour les corps très associés comme l'eau, ...

"Pour les mélanges, loin de la température critique la variation de la fluidité est encore linéaire. Mais plus on approche de la région critique, moins les formules linéaires sont exactes. Elles ne peuvent même plus prétendre à un semblant d'exactitude, ainsi que le montrent bien les lignes de fluidité des mélanges à concentrations voisines de la concentration critique: elles sont tout à fait courbes et concaves vers l'axe des températures. D'ailleurs, déj pour des concentrations éloignées de la concentration critique, au voisinage de la température de démixtion le coefficient de fluidité varie très fort. Mais le changement est plus graduel près de la concentration critique.

"Si l'on examine l'allure des isothermes de fluidité, on voit que pour les mélanges de corps normaux la loi d'additivité:

$$\varphi = a\varphi_1 + b\varphi_2$$

est assez bien satisfaite a des températures superieures à la température critique de dissolution. J'ai porté en abscisses les

conccntrations en poids, mais en prenant les concentrations en volume la loi d'additivité n'est pas mieux vérifiée. Ce n'est que

Fig. 37.—Fluidities of mixtures of cyclohexane and aniline at the critical-solution temperature. (*After Drapier.*)

dans le voisinage de la température critique qu'il se présente des écarts singuliers, résultant de la courbure des lignes d'egale concentration et se traduisant par une double inflexion des isothermes, . . ."

Commenting on the theory of v. Smoluchowski by way of explanation he remarks, "Il est probable que de pareilles hétérogénéités produirairent une augmentation de la viscosité et pourraient donc expliquer la courbure, toujours de même sens, des courbes d'égale concentration et par conséquent les écarts à loi d'additivité."

These researches make it perfectly clear that there is a decrease in the fluidity near the critical-solution temperature as predicted and that in some way this decrease is connected with the disappearance of homogeneity in the mixture. Most of the investigators have concerned themselves with the explanation of disappearance of homogeneity before the critical-solution temperature is reached, rather than of the increase in viscosity.
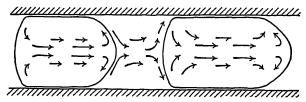
Fig. 38.—Diagram illustrating the flow of emulsions.

But we are here only interested in the fact that heterogeneity does occur simultaneously with the abnormal increase in viscosity, and not in the cause[1] of the heterogeneity itself.

Scarpa and Bose however offered explanations of the abnormal increase in the viscosity. In regard to Scarpa's assumption that the decrease in fluidity is due to the formation of hydrates, it is very possible that hydrates are formed between phenol and water, with which he worked; but he has not given any facts to prove that the hydration suddenly increases as the critical-solution temperature is approached even in this favorable case. In the cases studied by Drapier (cf. Fig. 34), such a chemical action seems to be out of the question, because if solvation occurred the fluidity-concentration curves would be sagged even above the critical-solution temperature.

In order to understand the explanation of Bose, we refer to Fig. 38 which may be taken to represent the hypothetical

[1] For an attempted explanation cf. Am. Chem. J., **33,** 1273 (1911).

appearance of the drops of an emulsion as they pass through a capillary tube. Due to the friction against the walls, the rear end of each drop is flattened and the front end is unusually convex. It is to be especially noted that when the drops are small in diameter as compared with the diameter of the tube and yet large enough to occupy the whole cross-section of the tube, the motion of the liquid is by no means entirely linear, being transverse as well as horizontal as indicated by the arrows. The effect of this transverse motion is to increase the apparent viscosity of the liquid. If, however, the drops are very large in comparison to the diameter of the tube, the importance of this transverse motion may become vanishingly small. Thus if the drops of an emulsion are large enough to fill the cross-section of a tube, the viscosity, as measured by the rate of efflux, will be at least as great as the sum of the component viscosities, but it may be greater due to the transverse motions. We grant that below the critical-solution temperature a part of the increase in viscosity may be due to these transverse motions, but Bose would seem to account for all of the abnormal increase in the viscosity in this way. This however is not warranted, for the reason that at the center of the capillary the liquid has normally a high velocity while at the boundary the velocity is zero, so that there is a considerable tendency for any drops to become disrupted and drawn out into long threads. It is impossible to believe that above the critical-solution temperature the surface tension of the "drops" is sufficient to prevent disruption, for we are accustomed to think that the surface tension at the critical temperature is zero, and the abnormality in the fluidity is a maximum at this temperature. We conclude therefore that neither the explanation of Scarpa nor of Bose is sufficient, but that the explanation based upon the nature of viscous flow in a heterogeneous mixture is both necessary and sufficient.

The theory requires that if the fluidities of the two components of the mixture are identical, it makes no difference whether fluidities or viscosities be considered additive; hence there should be no irregularity in the fluidity curves of such a pair of substances even in the vicinity of the critical-solution temperature. No case has been examined, so far as we know, in which the components have approximately the same fluidity and

the mixture has a critical-solution temperature. The nearest approximation is in the case of isobutyric acid, $\varphi_{20°} = 76.0$, and water, $\varphi_{20°} = 99.8$, examined by Friedländer. As can be seen from Fig. 39 taken from the work of Drapier, the irregularity is very slight. The calculated deviation is
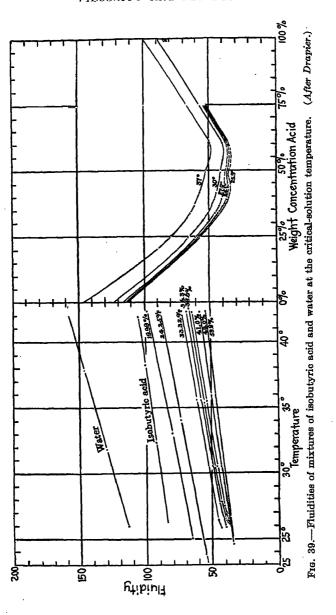
$$a\varphi_1 + b\varphi_2 - \frac{1}{a\eta_1 + b\eta_2} \tag{36}$$

which for a 50 per cent mixture corresponds to 27.6. The irregularity is greatest in the case of hexane, $\varphi_{20°} = 314.0$, and nitrobenzene, $\varphi_{20°} = 50.1$, where the fluidities are also the most unequal. The calculated deviation is in this case 95.6 for a 50 per cent mixture. The deviations actually read from the curves for isobutyric acid and water and hexane and nitrobenzene are of the order of 11 and 25 respectively. That these numbers are so much smaller than the calculated values may be easily accounted for on the supposition that the drops are not all sufficiently large to fill the cross-section of the capillary, and hence the viscosities are not strictly additive.

SUSPENSIONS

According to the view that viscosities are always additive, the viscosity of all suspensions should be infinite. On the contrary, as already stated, Friedländer found that colophonium suspended in water had practically no influence on the viscosity of water. Similarly Bose measured the viscosity of suspensions of finely-divided quartz, whose viscosity may be taken as infinite, in bromoform and water, and he found that the viscosity of the medium was but little changed. Had they measured the viscosities at increasing concentrations of the solid, they would have undoubtedly found that the viscosity was altered and in a perfectly definite manner. As already indicated, page 55 and Fig. 19, the fluidity curves of such suspensions are normally linear. Since, however, suspensions and emulsions are closely allied, it is important to inquire why viscosities are not additive in suspensions as well as in the emulsions already considered.

In suspensions, we have practically the same conditions as in emulsions in which the drops are so small that they do not nearly fill a cross-section of the capillary tube. In this case the viscosities are not strictly additive.

FIG. 39.—Fluidities of mixtures of isobutyric acid and water at the critical-solution temperature. (*After Drapier.*)

If for simplicity we imagine the solid particles of a suspension to be all united into sheets parallel to the direction of flow, as the shaded areas in Fig. 33 then it is evident that the flow will be the sum of the flows of the unshaded areas, *i.e.*, the fluidities will be strictly additive or

$$\varphi = a\varphi_1 + b\varphi_2 = b\varphi_2$$

since φ_1 is practically zero.

But if these solid sheets were broken up into fragments, one of which is shown as the cross-section of a cube at F in Fig. 40, the deformation of the liquid would tend to change the form of the cube into that of a parallelopiped as shown at G, but as the solid is rigid, this cannot take place; so that the shearing force can only rotate the cube around its center as shown at H. But
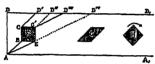
Fig. 40.—Diagram illustrating the flow of suspensions.

the failure of the solid to change its shape with the flow of the liquid will necessitate transverse motions in the liquid by way of readjustment, hence the viscosity of a suspension will always be greater than it would be were the fluidities strictly additive. If, as we believe can be proved to be the case, the amount of transverse motion in a suspension is proportional to the number of suspended particles of a given size, and for each particle the amount of transverse motion bears a constant ratio to the amount of shear, it will follow that the fluidity curves of suspensions must be linear, as has already been shown to be generally true (*cf.* p. 55 and Fig. 19).

Enough evidence has been given to indicate that the theory of the subject and the most diverse sorts of experimental data are in accord in supporting the fundamental hypothesis that fluidities are normally additive in homogeneous mixtures and fine suspensions, but not in heterogeneous mixtures. Much additional evidence could be given, but not without taking up subjects out of their natural order. This evidence will appear as we proceed. For further confirmation of these views *cf.* Drucker and Kassel (1911), White (1912).

James Kendall (1913), working in the Nobel Institute of Physical Chemistry under the direction of Professor Arrhenius, concluded that "the logarithmic viscosity (or fluidity) of a solu-

tion is the characteristic additive property, and not these quantities themselves." This conclusion was based upon data which for the reasons already given was not well suited for reaching a final decision of the matter. As the result of more recent study of the matter with Monroe (1919) and Wright (1920) Kendall has come to the conclusion that no formula tested by him will reproduce the observed data. The present author is in hearty accord with this conclusion of Kendall. It cannot be emphasized too strongly, to the novitiate particularly, that no single formula will reproduce faithfully any considerable portion of the observed data on the fluidity of mixtures. Moreover it is useless to look for such a formula in the present state of our knowledge. A much better plan is to assume the additivity of fluidities, which also has the virtue of being the simplest hypothesis that we can make, and then try to account for the deviations from the exact law on the basis of well-established physical and chemical evidence. If the fundamental hypothesis is incorrect, incongruities will soon develop to put us on the right track. If correct, we should proceed as rapidly as possible to exploit the new knowledge which fluidity measurements place in our hands.

CHAPTER II

FLUIDITY AND THE CHEMICAL COMPOSITION
AND CONSTITUTION OF PURE LIQUIDS

Attention was first strongly drawn to the desirability of study-
ing the viscosity of homogeneous liquids in relation to their other
properties by Graham in 1861. He himself measured the
viscosity of several organic liquids at the uniform temperature of
20° and noted that the times of flow increase with the boiling-
point, from which he inferred that there is a connection between
viscosity and chemical composition similar to that which exists
between the boiling-point and the chemical composition. By
comparing the times of flow of "equivalent amounts," obtained
by multiplying the times of flow of equal volume by the molecu-
lar weights and dividing by the density ($\eta M/\rho$), Rellstab (1868)
sought to gain a more intimate knowledge of this relation. He
measured the viscosity over a range of temperatures from 10 to
50° and then compared the substances at temperatures at which
their vapor-pressures are equal, as well as at a given temperature.
No simple quantitative relationship was found between his times
of flow and the molecular weight or vapor-pressure, but he stated
several qualitative relationships. Thus he noted that the time
of flow always decreases as the temperature rises, that an incre-
ment of CH_2 in a homologous series is in general accompanied
by an increase in the time of flow, but that metameric substances
may have very different efflux-times. Without attempting a
complete summary of his observations, the above suffice to show
that he regarded temperature, chemical composition and con-
stitution as all important in determining the rate of flow.

Přibram and Handl (1878–1881) studied a large number of
pure liquids over a range of temperatures from 10 to 60° express-
ing their results in "specific viscosities" taking water at 0° as 100.
Their researches marked a great step in advance but only to the
extent of confirming and extending the qualitative observations

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of Rellstab and also of Guerout, and not in establishing quantitative relationships.

Struck by the fact that metameric substances sometimes have such widely different viscosities, *e.g.*, isobutyl alcohol 0.03906 and ethyl ether 0.002345 at 20°, Brühl (1880) noted that the one with the higher viscosity generally had the higher boiling-point and index of refraction. But to this observation Gartenmeister (1890), testing a large number of substances at 20° or over a range of temperatures, found numerous exceptions.

It was at this point that Thorpe and Rodger (1894) decided to make an intensive study of the whole subject of the relation between the viscosity of liquids and their chemical nature. Their first care was to work out a method which would give them a far greater precision of measurement than had been obtained by many of their predecessors. They then carefully purified some 87 substances and measured their viscosities from 0°C to the boiling-point of each substance. An exhaustive search was then made for a basis of comparison which would bring out the quantitative connection between the viscosity and the chemical nature of the liquids. In this search they compared the viscosity coefficients (η), the "molecular viscosities" $[\eta(M/\rho)^{2/3}]$, the "molecular viscosity work" $(\eta M/\rho)$, and in order to make the comparison under comparable conditions they made the comparisons at the boiling temperatures, at "corresponding" temperatures, at temperatures where the slopes of the viscosity-temperature curves are equal, and at slopes varying under specified conditions. They furthermore compared the constants in the empirical equations which they found to best reproduce the observed viscosities as a function of the temperature, and they also compared the temperatures corresponding to a given slope in the viscosity-temperature curves. Their choice of temperatures of equal slope as a basis of comparison deserves a word in explanation. They found that on comparing the viscosity curves of substances which gave the best physico-chemical relationships at the boiling-point that the general shape of these curves was the same, or in other words the slopes of the substances at their boiling-points were practically identical. On the other hand, alcohols and other substances, which gave little evidence of physico-chemical relationships, had invariably a different

slope. It therefore occurred to them to compare their substances at temperatures of equal slope and they seemed to find theoretical justification in this proceeding, since at a given slope the temperature is exercising the same effect upon the viscosity of different substances, *i.e.*, $d\eta/dt$ is constant.

They were able to establish the most nearly quantitative relationship in the comparison between molecular viscosity work and chemical composition and constitution using a constant slope, arbitrarily selected as 0.000,032,3. We shall now examine the nature of this relationship.

By comparing the values for the homologues given in Table XXII they observed that the addition of a methylene group to a compound increases the observed value of the molecular viscosity work by $(80 \pm 5) \times 10^{-3}$ c.g.s. units. They assume that $CH_2 = 80$, the factor 10^{-3} being understood. Similarly an iso-grouping is found to lower the value observed for the normal compound by 8 ± 3 provided that the highly associated butyric acids are left out of the calculation.

The value of H_2 was found by subtracting the value of nCH_2, as calculated from the above constants, from the observed values of the paraffins whose general formula is C_nH_{2n+2} as shown in Table XXIII. The mean value of H_2 is -68 and since $CH_2 = 80$, $C = 148$.

Comparing normal propyl with allyl compounds, it was found that the occurrence of a double linkage and the loss of two hydrogen atoms lower the molecular viscosity work by 27 ± 1; hence the value of a double linkage was assumed to be -95.

Using the values thus obtained, they determined the value of oxygen in ketones to be -19, excluding acetic aldehyde and dimethyl ketone from the calculation because they are the first members of their respective series, and are probably associated. In the aliphatic acids the two oxygen atoms have a value of 81 ± 4, but since one of these is a carbonyl oxygen, the value of hydroxyl oxygen must be 100. On the other hand, oxygen when united as in ether was found to be 43. It seemed to them possible that oxygen might have yet other values such as the carbonyl oxygen in aldehydes as distinguished from ketones. Commenting on the different values which it seemed necessary to give to the same atom in differently constituted compounds, Thorpe

TABLE XXII.—MOLECULAR VISCOSITY WORK ($\eta M/\rho$) IN ERGS $\times 10^{-3}$ AT A SLOPE OF 0.000,032,3

Substance	Observed	Difference	Calculated	Difference, per cent
Pentane	329	86.0	332	−0.9
Hexane	415	80.0	412	0.7
Heptane	495	79.0	492	0.6
Octane	574		572	0.3
Isopentane	320	84.0	324	−1.2
Isohexane	404	78.0	404	0.0
Isoheptane	482		484	−0.4
Isoprene	284	72.0	278	2.1
Diallyl	356		358	−0.5
Methyl iodide	255	86.0	264	−3.5
Ethyl iodide	341	84.0	344	−0.9
Propyl iodide	425		424	0.2
Isopropyl iodide	417	88.0	416	0.2
Isobutyl iodide	505		496	1.8
Allyl iodide	399		397	0.5
Ethyl bromide	282	71.0	277	1.8
Propyl bromide	353	87.0	357	−1.1
Isopropyl bromide	346		349	
Isobutyl bromide	433		427	1.4
Allyl bromide	327		330	−0.9
Ethylene bromide	450	76.0	456	−1.3
Propylene bromide	526	88.0	536	−1.9
Isobutylene bromide	614		608	1.0
Acetylene bromide	418		409	2.0
Propyl chloride	294		295	−0.3
Isopropyl chloride	290	74.0	287	1.0
Isobutyl chloride	364		367	−0.8
Allyl chloride	268		268	0.0
Methylene chloride	241	85.0	244	−1.2
Ethylene chloride	326		324	0.6
		76.5		
Methyl sulfide	240		236	1.7
Ethyl sulfide	393		396	−0.8
Methyl ethyl ketone	302	81.0	301	0.3
Methyl propyl ketone	383		381	0.5
Diethyl ketone	376		381	−1.3
		77.0		
Formic acid	160	86.0	159	0.6
Acetic acid	237	74.0	239	−0.8
Propionic acid	323		319	1.2
Butyric acid	397		399	−0.5
Isobutyric acid	398		391	1.8
Acetic anhydride	394	74.0	393	0.3
Propionic anhydride	542		553	−2.0
Ethyl ether	295		295	0.0
Benzene	314	81.0	315	−0.3
Toluene	395	80.0	395	0.0
Ethyl benzene	475		475	0.0
Ortho-xylene	483		475	1.7
Meta-xylene	474		475	−0.2
Para-xylene	467		475	−1.7

TABLE XXIII.—THE VALUE OF HYDROGEN

Substance	n	$C_{n2}H_{n+2}$	nCH_2	H_2
Normal paraffins	5	329	400	−71
	6	415	480	−65
	7	495	560	−65
	8	574	640	−66
Iso-paraffins......	5	320	392	−72
	6	405	472	−67
	7	482	552	−70

and Rodger remark (p. 643), "If such differences are confirmed by more numerous observations, viscosity will rank as one of the most useful properties in determining the constitution of oxygen compounds." They then add, "It is, of course, to be remembered here that the value of hydroxyl oxygen as it is derived from the acids is no doubt affected by molecular complexity."

Using the constants obtained as above, and grouped together in Table XXIV for reference, Thorpe and Rodger calculated the values of the molecular viscosity work for the substances given in Table XXII, and reproduced in column 4. The average difference between the observed and calculated values is less than 1 per cent, but it is to be remarked that water and the alcohols do not enter into comparison at this particular slope. At a different slope they were able to bring these substances into the comparison, and they found a very great divergence between the observed and calculated values amounting to 44 per cent in the case of dimethyl ethyl carbinol and 47 per cent in that of water. Again the difference was partly attributable to constitutive influences, since it was noted that the divergence is least in the primary and greatest in the tertiary alcohols. But at the same time they note that these compounds are most certainly associated and the theoretical values of the molecular weight were used in place of the actual values. They conclude their study of molecular viscosity work at equal slope with the following noteworthy statement: "The results here obtained are of precisely the same nature as those discussed under molecular viscosity. More detail has been given to show that the substances which give deviations from the calculated values fall

into two classes. In the first the deviations are to be attributed to chemical constitution, as similar disturbing effects may be detected in the magnitudes of other physical properties which do not seem to be affected by molecular complexity. In the second are those substances like the acids, water, and the alcohols, for which the disturbing factor is, no doubt, molecular complexity, the effect produced in this way, in the case of the alcohols, being dependent upon their chemical nature." Thorpe and Rodger have done great service in stating the problem before us so clearly. At a subsequent point in our discussion, we will show how by a different method of comparison it is possible to largely avoid the first cause of discrepancy given above, and how then with only one unknown quantity remaining, it is possible to get a proximate solution of the problem.

TABLE XXIV.—MOLECULAR VISCOSITY WORK CONSTANTS AT SLOPE 0.000,032,3

Hydrogen	− 34
Carbon	148
Hydroxyl-oxygen, C-O-H	100
Ether-oxygen, C-O-C	43
Carbonyl-oxygen, C = O	− 19
Sulfur, C-S-C	144
Chlorine (in monochlorides)	89
Chlorine (in dichlorides)	82
Bromine (in monobromides)	151
Bromine (in dibromides)	148
Iodine	218
Iso-grouping	− 8
Double linkage	− 95
Ring-grouping	−369

The effect of chemical constitution upon viscosity has been employed to good effect in the solution of several much-mooted chemical problems by Dunstan and Thole and their co-workers. Thus Thole (1910) observed a steady increase in the viscosity of freshly distilled ethyl acetoacetate owing to the gradual enolization of the ketonic form. Hilditch and Dunstan (1911) have observed that the presence of Thiele's "conjugated double bonds" in compounds produces a great increase in the viscosity. Thole (1912) has shown that the viscosity method can be used to distinguish between geometrical isomerides like maleic and fumaric

acids.   But while they attribute these effects to the constitution
of the molecules, it should be noted that the immediate cause of
the increase in viscosity may in each case be *association,* which
is the same as saying that it may be due to chemical composition
as distinguished from chemical constitution.   Certainly com-
pounds containing the hydroxyl radical are often associated and
these same compounds are noted for their high viscosity, so that
in the case of ethyl acetoacetate the way seems open to explain
the greater viscosity of the enol form on the basis of an associated
molecule, quite as well as on the basis of symmetry or other
constitutive influence.   At first sight it seems as though consti-
tutive influences must solely and immediately determine the
viscosity values in each of the above examples, but Thole (1912)
seems to realize that this is not the actual case with maleic and
fumaric acids, the latter of which gives the higher viscosity in
methyl alcohol solution.   He says, "The viscosities of the isomers
depend not only on the relative positions of the unsaturated
groups but also on the degree of residual affinity" which causes
molecular association.   Thus the "adjacent" maleic acid may
have the lower viscosity due to slighter association.   This view
is borne out by the fact noted by Thole that "barium fumarate
crystallizes with three molecules of water while barium maleate,
in which the residual affinities of the carboxyl groups are more
nearly mutually satisfied, combines with only one molecule of
water."

To what extent different constitutive influences affect the
association of compounds is an exceedingly important subject
but it is not relevant to our discussion of viscosity.   Our problem
is to study the *immediate* effects of constitutive influences and
the chemical composition of the molecule upon the viscosity and
to estimate their relative importance.

Regardless of how much uncertainty there may be in regard
to the importance of constitutive influences on viscosity, there
can be no doubt about the importance of chemical composition.
All evidence shows that this factor is of great importance.   Dun-
stan and Langton (1912) have made use of this for the determina-
tion of transition points, and Thole (1913) in the detection of the
presence of racemic compounds in the liquid state, and many other
instances might be cited.

Comparison of Fluidities.—We have already given reasons for believing that if liquids were completely unassociated and expanded in a linear manner with the temperature, the fluidity-temperature curves would be straight lines. To compare a family of curves which are straight lines is a simpler task than the comparison of a family of hyperbolas, hence it seems a justi-
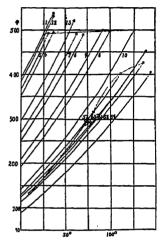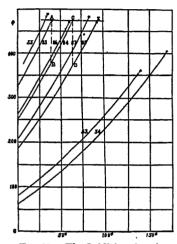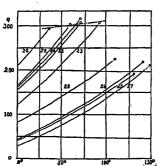
Fig. 41.—The fluidities of various hydrocarbons at different temperatures and extrapolated to their boiling temperatures. 4. Pentane; 5. Isopentane; 6. Hexane; 7. Isohexane; 8. Heptane; 9. Isoheptane; 10. Octane; 11. Trimethylethylene; 12. Isoprene; 13. Diallyl; 56. Benzene; 57. Toluene; 58. Ethylbenzene; 59. (*o*)-Xylene 60. (*m*)-Xylene; 61. (*p*)-Xylene.

Fig. 42.—The fluidities of various ethers and acid anhydrides at different temperatures and extrapolated to their boiling temperatures. 53. Acetic anhydride; 54. Propionic anhydride; 55. Diethyl ether; 83. Methyl propyl ether; 84. Ethyl propyl ether; 85. Dipropyl ether; 86. Methylisobutyl ether; 87. Ethylisobutyl ether.

fiable expectation that we may be able to find simpler relations by a suitable comparison of fluidities. Before deciding on a basis of comparison let us inspect the fluidity-temperature curves as obtained from the observations of Thorpe and Rodger as given in Figs. 41 to 46. Confining our attention first of all to the aliphatic hydrocarbons in Fig. 41 we see that near their boiling-points, indicated by small circles in the figure, the fluidity
8

curves are nearly straight and parallel lines. However as we get away from the boiling-temperature, there is a curvature present so that it is probable that the fluidity curve would reach the temperature axis asymptotically as the temperature were lowered. Broadly speaking, the curves of a given homologous series near their boiling-points consist of a series of parallel straight lines, which are therefore completely defined mathematically by their slopes and intercepts. We find the same thing in other series,

FIG. 43.—The fluidities of various bromides at different temperatures. 20. Ethyl bromide; 21. Propyl bromide; 22. Isopropyl bromide; 23. Isobutyl bromide; 24. Allyl bromide; 25. Ethylene bromide; 26. Propylene bromide; 27. Isobutylene bromide; 28. Acetylene bromide.
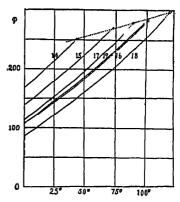
FIG. 44.—The fluidities of various iodides at different temperatures. 14. Methyl iodide; 15. Ethyl iodide; 16. Propyl iodide; 17. Isopropyl iodide; 18. Isobutyl iodide; 19. Allyl iodide.

as the ethers and acid anhydrides given in Fig. 42, but it is clear that the slope is different in the two classes. The slope then is dependent upon the class to which a compound belongs and the intercepts are dependent upon the chemical composition. According to this broad aspect of the case it should make no difference whether we compare fluidities at a given temperature or temperatures corresponding to a given fluidity. But there are several reasons for choosing the latter basis of comparison rather than the former.

1. The slopes of the fluidity-temperature curves for a given homologous series are more nearly the same when the fluidities are equal.

2. When the fluidities are the same, the vapor-pressures are nearly equal, and experience has shown that substances are comparable at temperatures which correspond to equal vapor-pressure.

3. The fluidity curves of associated substances like the alcohols, Fig. 46, depart widely from linearity at low fluidities, although they approach linearity at high fluidities, as do the curves of other compounds.

4. A yet more cogent reason grows out of the fact that exact
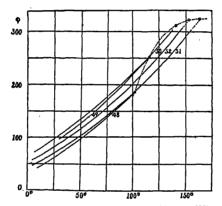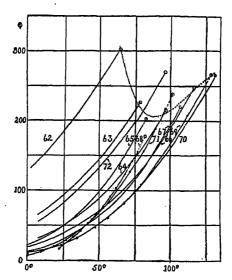
FIG. 45.—The fluidities of various organic acids at different temperatures. 48. Formic acid; 49. Acetic acid; 50. Propionic acid; 51. Butyric acid; 52. Isobutyric acid.

parallelism in the curves of a given class is not to be expected since all fluidity-temperature curves must undoubtedly meet at the absolute zero of temperature. Hence while it may require a constant increment of temperature to produce a given fluidity as each methylene group is added to the molecule, it is absolutely certain that a constant decrement of the fluidity at a given temperature cannot be expected as each methylene group is added. Thus a methylene group added to pentane, Fig. 37, lowers the fluidity at 0° by a certain amount, but the effect of adding a

methylene group to heptane is less and the effect of adding other methylene groups must be still less, otherwise it would require no very high molecular weight to give a negative fluidity, which is inconceivable.

The fluidity of 200 is chosen as a basis of comparison in order that as large a number of substances as possible may be included. The absolute temperatures and slopes of several unassociated

Fig. 46.—The fluidities of various alcohols at different temperatures. 62. Methyl alcohol; 63. Ethyl alcohol; 64. Propyl alcohol; 65. Isopropyl alcohol; 66. Butyl alcohol; 67. Isobutyl alcohol; 68. Trimethyl carbinol; 69. Active amyl alcohol; 70. Inactive amyl alcohol; 71. Dimethylethylcarbinol; 72. Allyl alcohol.

compounds corresponding to the fluidity of 200 are given in Table XXV. The third column of this table shows that the value of a methylene grouping varies around a mean value of 22.7, the mean deviation from this value being 3. The effect of an iso-grouping is to decrease the temperature required by about 7.6°, as shown in Table XXVI.

TABLE XXV.—ABSOLUTE TEMPERATURES AND SLOPES OF NON-ASSOCIATED SUBSTANCES CORRESPONDING TO A FLUIDITY OF 200 C.G.S. UNITS

Substance	Absolute temperature (ϕ = 200) observed	Difference CH_2	Slope at (ϕ = 200)	Absolute temperature (ϕ = 200) calculated	Per cent, difference
Hexane...............	$(255.1)^1$		(2.88)	254.6	0.2
Heptane..............	276.1	(21.0)		277.3	0.4
Octane...............	299.1	23.0	2.44	300.0	0.3
Isohexane............	(249.0)		(2.79)	247.0	0.8
Isoheptane...........	269.2	(20.2)	2.68	269.7	0.2
Methyl iodide.........	290.2	19.0	1.92	287.4	1.0
Ethyl iodide..........	309.2		1.80	310.1	0.3
Propyl iodide.........	332.7	23.5	1.82	332.8	0.0
Isopropyl iodide.......	324.5		1.92	325.2	0.2
Isobutyl iodide........	345.5	21.0	1.86	347.9	0.7
Allyl iodide...........	330.5		1.82	328.8	0.5
Ethyl bromide........	268.7		2.22	273.5	1.8
Propyl bromide.......	296.6	27.9	2.08	296.2	0.1
Isopropyl bromide......	289.4		2.22	273.5	1.8
Isobutyl bromide.......	315.0	25.6	2.08	311.3	1.1
Ethyl propyl ether......	(255.0)		(2.70)	256.1	0.5
Dipropyl ether........	279.0	(24.0)	2.62	278.8	0.1
Methylisobutyl ether...	(251.1)		(2.75)	248.5	1.0
Ethylisobutyl ether.....	270.1	(19.0)	2.68	271.2	0.4

[1] Values in parentheses are extrapolated.

TABLE XXVI.—THE VALUE OF THE ISO-GROUPING

Substance	Temperature observed, normal grouping	Temperature observed, iso-grouping	Difference
Hexane...........	255.1	249.0	6.1
Heptane..........	276.1	269.2	6.9
Propyl iodide.....	332.7	324.5	8.2
Propyl bromide...	296.6	289.4	7.2
Propyl chloride....	261.5	255.2	6.3
Butyric acid......	381.6	371.6	10.0
Methyl butyrate..	304.2	295.8	8.4

The value for the hydrogen atom is calculated as follows:

TABLE XXVII.—THE VALUE OF THE HYDROGEN ATOM

Substance	Temperature observed	$n\mathrm{CH_2}$ calculated	Difference
Hexane............	255.1	136.2	118.9
Heptane..........	276.1	158.9	117.2
Octane...........	299.1	181.6	117.5
Isohexane........	249.0	128.6	120.4
Isoheptane........	269.2	151.3	117.9

The value for H_2 is 118.4 ± 1.0. The hydrogen atom has therefore a value of 59.2 and the carbon atom of -95.7.

The value of the "double bond" in allyl compounds is obtained from Table XXVIII.

TABLE XXVIII.—THE VALUE OF THE DOUBLE BOND

Substance	Temperature observed, normal propyl	Temperature observed, allyl	Difference
Iodides...........	332.7	330.7	2.2
Bromides.........	296.6	292.2	4.4
Chlorides.........	261.5	256.0	5.5

To raise the fluidity of an allyl compound to 200 it is only necessary to raise it to a temperature which is some 4° lower than is necessary for the corresponding normal compound, containing two more hydrogen atoms. Thus the "double bond" has a value of 114.4, the absence of the hydrogen atoms being nearly compensated for by the "condition of unsaturation."

Assuming that the ethers are unassociated, we may obtain the value of the oxygen atom.

TABLE XXIX.—THE VALUE OF THE OXYGEN ATOM

Substance	Temperature observed	C_nH_{2n+2}	Oxygen
Ethylpropyl ether.............	254.9	231.9	23.0
Dipropyl ether................	279.0	254.6	24.4
Methylisobutyl ether...........	251.4	224.3	27.1
Ethylisobutyl ether............	270.3	247.0	23.3

This gives an average value for oxygen of 24.2 with an average divergence of 1.3 from this mean. From these values, the absolute temperatures corresponding to a fluidity of 200 may be calculated. Some of these calculated values are given in the fifth column of Table XXV. A comparison between these calculated and the observed values for 35 substances shows an average percentage difference of less than 0.8 per cent.

Association.—In attempts to establish a relation between viscosity and chemical composition it has been customary to disregard entirely the fact that certain classes of substances are known to be highly associated, and hence the molecular values as calculated from the atomic constants cannot be expected to agree with the observed values. A more logical method of procedure would be to use known values of the association in arriving at the calculated *molecular temperatures*. The difficulty of this method is that the values of the association as given by different methods do not agree very closely and even the methods of getting these values have been subjected to criticism. It seems best therefore to reverse the method and use our atomic constants to calculate the association, which can then be compared with the values of the association obtained from the surface tension, volume, *et cetera*.

In the calculation of the atomic constants as given above, it was assumed that the compounds chosen were non-associated. This is not entirely warranted, but they must be associated to approximately the same extent since the agreement between the calculated and observed values is generally satisfactory, and it is the general belief that some of these compounds are indeed unassociated. It is highly probable that association or constitution is responsible, in part at least, for the uncertainty in the so-called "constants," but this uncertainty can be removed by further amplification of our data.

Since the atomic constants are additive, it follows directly that the association will be given by the ratio of the observed to the calculated values of the temperature corresponding to the given fluidity. Thus for water $(H_2O)_x$ at the fluidity of 200 the absolute temperature is 328.9, while the value calculated from the gas formula H_2O is $2 \times 59.2 + 24.2 = 142.6$. The association factor (x) at the temperature of observation (328.9°

absolute) is therefore $328.9/142.6 = 2.31$. In Table XXX are given the observed and calculated absolute temperatures corresponding to the fluidity of 200 and the association calculated therefrom for some typical associated compounds. The slopes of these curves are also given in the fourth column.

TABLE XXX.—ABSOLUTE TEMPERATURES AND SLOPES OF SOME ASSO-
CIATED COMPOUNDS CORRESPONDING TO A FLUIDITY OF 200 C.G.S. UNITS

Substance	Absolute temperature for ($\phi = 200$) observed	Absolute temperature for ($\phi = 200$) calculated	Slope for ($\phi = 200$)	Association
Water................	328.9	142.6	3.04	2.31
Formic acid..........	(380.2)	185.5	(2.18)	2.05
Acetic acid...........	363.8	208.2	2.06	1.77
Propionic acid........	362.0	230.9	1.92	1.57
Butyric acid..........	381.6	253.6	1.92	1.57
Isobutyric acid.......	371.6	246.0	2.00	1.51
Methyl alcohol.......	305.2	165.3	2.78	1.84
Ethyl alcohol........	343.4	188.0	3.24	1.83
Propyl alcohol........	365.6	210.7	3.76	1.74
Butyl alcohol........	377.0	233.4	3.44	1.62
Ethyl formate........	273.8	230.7	2.40	1.19
Ethyl acetate........	284.0	253.4	2.50	1.12
Ethyl propionate......	298.1	275.1	2.44	1.08

The test of our complete process of reasoning comes now when we compare the association obtained in this way with the values which have been obtained by other methods. The results of this comparison are shown by Table XXXI.

So far as one is able to judge, the result seems to be all that could be desired. There are almost invariably values given by other methods which are both higher and lower than our values and such a degree of association is certainly not inconsistent with our knowledge of the chemical conduct of these substances. The fluidity method of obtaining the association factor seems to be freer from assumptions, to which questions may be raised, than other methods which have been proposed, and it is to be hoped that it may prove useful in calculating this very important factor. If eventually we are able to obtain thoroughly consistent

TABLE XXXI.—A COMPARISON OF THE VALUES OF ASSOCIATION AS DETERMINED BY DIFFERENT INVESTIGATORS

Substance	R. & S.,[1] 16–46°	R. & S., corrected by Traube	Traube,[2] 15°	Longinescu[3]	B. & H.,[4] temperature of (ϕ = 200)
Water................	3.55 / 1.64	1.79	3.06	4.67	2.31
Dimethyl ketone.........	1.26	1.18	1.53	1.60	1.23
Diethyl ketone..........	....	....	....	1.25	1.16
Methyl propyl ketone...	1.11	1.10	1.43	1.25	1.14
Formic acid.............	3.61	2.41	1.80	1.80	2.05
Acetic acid.............	3.62 / 2.13	2.32	1.56	1.75	1.77
Propionic acid..........	1.77	1.45	1.46	1.55	1.57
Butyric acid............	1.58	1.35	' 1.39	1.86	1.51
Isobutyric acid..........	1.45	1.28	. 1.31	....	1.51
Benzene................	1.01	1.05	1.18	....	>1.17 <1.31
Toluene................	0.94	1.01	1.08	....	>1.08 <1.517
Methyl alcohol..........	3.43 / 2.32	2.53	1.79	3.17	1.84
Ethyl alcohol............	2.74 / 1.65	1.80	1.67	2.11	1.83
Propyl alcohol...........	2.25	1.70	1.66	1.67	1.74
Isopropyl alcohol........	2.86	2.00	1.53	....	1.75
Butyl alcohol...........	1.94	....	....	1.47	1.62
Isobutyl alcohol.........	1.95	1.53	1.54	....	1.66
Active amyl alcohol......	1.97	1.54	1.53	....	1.54
Allyl alcohol............	1.88	1.50	1.55	1.80	1.69
Methyl formate.........	1.06	1.07	(1.60)	1.12	1.25
Ethyl formate...........	1.07	1.08	$1.39_0°$	....	1.19
Methyl acetate..........	1.00	1.04	$1.48_0°$	1.09	1.17
Ethyl acetate...........	0.99	1.04	1.25	1.00	1.12
Propyl acetate..........	0.92	1.00	1.31	1.00	1.11
Ethyl propionate........	0.92	1.00	1.27	0.94	1.08
Methyl butyrate........	0.92	1.00	$1.30_0°$	1.00	1.10

[1] RAMSAY and SHIELDS, *Zeitschr. f. physik. Chem.*, **12**, 464 (1893); **15**, 115 (1894).
[2] TRAUBE, *Ber. d. deutsch. chem. Gesell.*, **30**, 273 (1897).
[3] *J. chim. Phys.*, **1**, 289 (1903).
[4] BINGHAM and HARRISON, *loc. cit.*

results from the different methods, it is interesting to observe that it should be possible to calculate the volume, surface tension, *et cetera*, even of associated liquids from their atomic constants and their fluidities.

Fluidity and Chemical Constitution.—Dunstan and Thole (*Viscosity of Liquids*, page 31) have very properly called attention to the fact that the differences between the calculated and observed values of the fluidity in Table XXV "are due not only

to association but to want of sufficient data for calculating accurately the atomic 'constants' and also to constitutional effects, such as the mutual influence of groupings in the molecule, symmetry and so forth." As was intimated earlier in this chapter, to chemical constitution has generally been attributed a very large effect on viscosity, but it often turns out on investigation that this supposed constitutive influence occurs in substances that are known to be associated and this association was not taken into account, and in other cases the supposed constitutive influence is almost certainly purely a hypothesis framed to explain an unnoticed defect in the method of comparison. We shall now give some facts to support these bare statements and we shall then investigate the important question as to whether this dwindling constitutive effect, as distinct from the effect of association, can safely be disregarded altogether.

In assigning values to the halogen atoms, Thorpe and Rodger (p. 669 *et seq.*) found it necessary to give a different value to chlorine in monochlorides, dichlorides, trichlorides and tetrachlorides, but even then the results are not satisfactory since in ethylene and ethylidene chlorides the value which must be assigned the chlorine atom is certainly different. How the effect of the chlorine atom varies at the fluidity of 200 is shown in the fourth column of Table XXXII.

TABLE XXXII.—THE VALUE OF THE CHLORINE ATOM
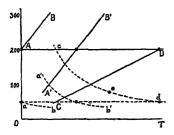
Substance	Absolute temperature (ϕ = 200), observed	Hydrocarbon residue, calculated	Chlorine	Association
Propyl chloride.......	261.5	127.3	134.2	1.105
Isopropyl chloride.....	255.2	119.7	135.5	1.11
Isobutyl chloride......	285.2	142.4	142.8	1.13
Allyl chloride.........	256.0	123.3	132.7	1.10
Ethylene chloride.....	336.5	45.4	145.5	1.27
Ethylidene chloride....	291.2	45.4	122.9	1.10
Methylene chloride....	279.1	22.7	128.7	1.15
Chloroform..........	305.3	− 36.5	113.9	1.04
Carbon tetrachloride..	347.0	− 95.7	110.7	1.01
Carbon dichloride.....	356.3	− 77.0	108.3	0.99

There is then a somewhat regular decrease in the apparent value of chlorine as the number of atoms in the molecule are increased. How much of this is due to constitutive influence directly and how much can be explained on the ground of association? Ramsay and Shields and Traube agree that carbon tetrachloride is very little associated if at all, Ramsay and Shields giving the value 1.01 and Traube $1.00_{15°}$. If then we take the average of the closely agreeing values of the two compounds containing four chlorine atoms we obtain as the value of the chlorine constant 109.5 and with this we can calculate the association of the other compounds. The values thus obtained are given in the fifth column of Table XXXII. Ethylene chloride is seen according to this method of calculation to be highly associated, but Traube has given a still higher value for the association at 15° of 1.46. Data for the other chlorides is lacking, but calculating the association of propyl chloride by the method of Traube, the author obtains the value of 1.11 which agrees excellently with our value of 1.105. The mono-halides seem to be usually associated according to Traube for he gives for methyl iodide 1.30, for ethyl iodide 1.19 and for ethyl bromide 1.28. It is greatly to be regretted that our available data is so meager, but for the present we can only conclude that the effect of constitution upon the value of the chlorine atom is too small to be detected.

In reference to the lack of constancy in the value of a methylene group in Table XXV, it seemed desirable to take the average of as large number of values as possible, but with the limited data on hand this made it necessary to include a number of compounds which are certainly associated. This does not mean that the value of the methylene group is therefore certainly in error because associated compounds can give this as well as others, provided the homologues are *equally* associated; and even if they are unequally associated, the average value for the methylene grouping may not be greatly in error although the individual differences may be large. Finally the fact that the calculated values in Table XXV differ from the observed values by less than 1 per cent seems to put a maximum limit upon certain kinds of constitutive influences.

Hitherto it has been deemed necessary to give oxygen a differ-

ent value depending upon whether the oxygen was in a carbonyl group, hydroxyl, ether, *et cetera*. We will now attempt to show that this was necessary so long as viscosities formed the basis of comparison, but it was *not* an evidence of constitutive influence, and in comparing *fluidities* only *one* value for oxygen is obtained irrespective of the manner in which it is combined, and yet we have seen that satisfactory association factors are obtained. Let AB and $A'B'$ in Fig. 47 represent two fluidity curves, parallel to each other and therefore presumably representing members of the same class of substances, and let a third fluidity curve CD be at an angle to the other two to represent a substance in another class. Since we have elected to compare absolute

Fig. 47.—Diagram illustrating the relationship between viscos-ity- and fluidity-temperature curves.

temperatures at a fluidity of 200, this amounts to comparing the intercepts of the curves on the line AD, whose equation is $\varphi = 200$. The corresponding viscosity curves obtained by taking the reciprocal values of the above fluidities and multiplying by 10,000 are represented by ab, $a'b'$, and cd; and ad is of course the reciprocal of the line AD. But the point a and the point where the curve $a'b'$ crosses ad are points of equal slope on the viscosity curves, hence within a given class it makes no great difference whether we compare temperatures corresponding to a given fluidity or temperatures corresponding to a given slope on the viscosity curves. The latter is exactly the method of comparison which Thorpe and Rodger found very advantageous. But between different classes they found difficulties which they attributed to constitutive influences. But their difficulty is now easily explained, for d is the true reciprocal of the point D which we believe should be used in the comparison; on the other hand, they selected the point e, which has the same slope as the point a, and for this choice we think that there is not adequate reason.

It has been customary to assume that different kinds of groupings should have special values assigned to them, and particularly important among these was the "ring grouping."

But it is not clear that this is unavoidable, for in the case of benzene we note that the compound differs from hexane by eight hydrogen atoms, and since we found in the allyl compounds that the absence of a pair of hydrogen atoms is compensated for to the extent of 114.4 we obtain for the calculated value, $59.2 \times 6 - 95.7 \times 6 + 114.4 \times 4 = 238.6$. The observed value is 311.9; hence the association is 1.30, which is somewhat larger than the value obtained by Traube of 1.18. It has usually been believed that the more compact and symmetrical the molecule was, the lower would be the temperature required to give it a certain fluidity. In disregarding constitutive influences entirely for the time being, as we have done here, we suppose that benzene would require the same temperature as a straight chain hydrocarbon containing four "double bonds." If Traube's value of the association or some other value less than 1.30 is correct, we will be compelled to assign a positive value to the ring grouping in order to increase the calculated value. In other words, the evidence at hand indicates that the effect of the ring grouping is not to make the compound less viscous but more so. This is so contrary to earlier belief and to the probabilities of the case that it seems preferable to await further data before assigning any value to the ring grouping.

Having been unable to detect the effect of constitutive influences upon fluidity with the data at hand in the halogen, oxygen, or ring compounds, we have left remaining one positive evidence in the value which we have found it necessary to give to the "iso-grouping." This effect is not large but it is fairly uniform and quite outside of the observational error. We cannot believe that normal hexane and heptane are sufficiently associated to account for the higher temperature above their isomers required to give them a fluidity of 200. If then an iso-grouping affects fluidity it is probable that there are other constitutive influences, but the solution of this problem evidently requires more data, particularly among the higher homologues. In this connection the reader should have regard for the relation of fluidity to volume, to be discussed later.

Before closing the chapter on fluidity and chemical composition and constitution, we may add that constants calculated for a fluidity of 300 give an association which is invariably a little

lower than at a fluidity of 200.   This is as one would expect.
From these values of the association the temperature coefficient
of the association factor can be obtained.   (Bingham (1910),
page 306.)

From the constants at different fluidities one may conceivably
obtain a series of points on the fluidity-temperature curve
heretofore unknown perhaps, and using these points the whole
curve may evidently be drawn.

The constants for fluidities 200 and 300 are for convenience
grouped together in Table XXXIII.

TABLE XXXIII.—TEMPERATURE CONSTANTS AT FLUIDITY 200 AND
FLUIDITY 300

Atom or grouping	$\varphi = 200$	$\varphi = 300$
Carbon...............	−95.7	−110.2
Hydrogen.............	59.2	67.8
Oxygen...............	24.2	27.1
Iso..................	−7.6	−8.2
Double bond..........	114.4	131.3
Sulfur...............	76.5	
Chlorine.............	109.5	

CHAPTER III

FLUIDITY AND TEMPERATURE, VOLUME AND PRESSURE; COLLISIONAL AND DIFFUSIONAL VISCOSITY

We have established in the preceding chapter that the viscosity of a substance is closely dependent upon the magnitude of the molecules making up the substance. In this and succeeding chapters we will investigate the relation between viscosity and various physical properties.

Temperature.—Prior to 1800, water was considered to be perfectly fluid, but by causing equal volumes of water at corresponding pressures to flow through tubes of given dimensions Gerstner in that year proved that the fluidity (Flüssigkeit) of water varies considerably with the temperature.

We have already seen that Poiseuille expressed this change in the form of the parabolic equation

$$K = a + bT_c + cT_c^2. \tag{36}$$

After viscosity had been defined, O. E. Meyer (1861) introduced the viscosity coefficient into the formula which then became

$$\eta = \frac{\eta_o}{1 + \alpha T_c + \beta T_c^2} \tag{37}$$

where η_o is the viscosity at 0°C and T_c is the temperature Centigrade. In spite of the fact that the two equations are not interchangeable, the latter formula is usually associated with the name of Poiseuille. We will refer to it as the Meyer-Poiseuille formula. It holds for water from 0 to 45° with a maximum deviation of 1 per cent. For temperatures above 45° Meyer and Rosencranz (1877) proposed the formula

$$\eta = \frac{\eta_o}{1 + \alpha T_c} \tag{38}$$

Various investigators have employed the Meyer-Poiseuille formula and confirmed the fact of its limited applicability. We may mention Grotrian (1877), Noack (1886), Thorpe and Rodger (1893), Knibbs (1895).

In 1881 Slotte gave a formula to cover the entire range of viscosities from 0 to 100°

$$\eta = \frac{a - bT_c}{c + T_c} \tag{39}$$

or

$$\eta = \frac{\alpha}{\beta + T_o} - \gamma, \tag{40}$$

which accords with the values of Sprung to 0.7 per cent.

Most of the formulas which have been proposed have been applied primarily to water. But Koch (1881) and Wagner (1883) found that a formula of a different type is necessary for mercury and Koch proposed the formula

$$\eta = \alpha + \beta T_o + \gamma T_c{}^2 + \partial T_c{}^3 \tag{41}$$

which holds from -20 to 340°C with a maximum deviation of less than 2 per cent. But Slotte has applied the much simpler formula of Meyer and Rosencranz with good results. On the other hand, Batschinski (1900) has given a formula for mercury

$$\eta = \frac{a}{T} + b + cT \tag{42}$$

where T is the temperature absolute. As a first approximation

$$\eta T = a, \tag{43}$$

which can be deduced from Jaeger's theory of fluid friction.

Graetz (1883–5) is one of the few who have attempted to derive a formula from theoretical considerations. We may therefore give his argument in some detail.

According to Maxwell (1868) the viscosity of a body is the product of two factors, the modulus of rigidity E and the time of relaxation τ. The time of relaxation was defined as the time necessary for the strain after deformation in a body to sink to $1/E$ of its original value. The reciprocal of the time of relaxation is called the relaxation number, n, or

$$n = \frac{1}{\tau}$$

This is the number of times per second that the strain will sink to $1/E$ per second if the strain is renewed. For absolutely rigid solids the value of τ is infinite and for ductile solid bodies which show elastic after-effect the relaxation may continue for hours or days. But if, through raising the temperature, the substance is

changed to a liquid or gas, the time of relaxation becomes smaller and smaller, and for air Maxwell has given the value

$$\tau = 1/5{,}099{,}100{,}000 \text{ sec.}$$

With rising temperature, the value of τ increases, and according to Graetz, one may write

$$n = n_1\vartheta + n_2\vartheta^2 + n_3\vartheta^3 + \ldots$$
$$= n_1\vartheta(1 + \alpha_1\vartheta + \alpha_2\vartheta^2 + \ldots)$$

where ϑ is the temperature reckoned from the temperature at which the viscosity is infinite, *i.e.*, the temperature of solidification.

In gases the modulus of rigidity is known to be equal to the gas pressure at the critical temperature and is of the order of magnitude of a hundred atmospheres. In solids, where the modulus of rigidity is known, it has a value from 100,000 to 1,000,000 atmospheres. Since E decreases in passing from the solid through the liquid into the gaseous condition, its value approaches the critical pressure P at the critical temperature ϑ_0, and we have according to Graetz

$$E = P + b_1(\vartheta_0 - \vartheta) + b_2(\vartheta_0 - \vartheta)^2 + b_3(\vartheta_0 - \vartheta)^3 + \ldots$$

where $b_1, b_2, b_3, \ldots$ are constants.

From Maxwell, we get

$$\eta = E\tau = \frac{E}{n}$$

or

$$\eta = \frac{P + b_1(\vartheta_0 - \vartheta) + \ldots}{n_1\vartheta(1 + a_1\vartheta + a_2\vartheta_2 + \ldots)}$$
$$= a\frac{\vartheta_0 - \vartheta}{\theta}(1 + \beta_1\vartheta + \beta_2\vartheta^2 + \ldots)$$

where $a, \beta_1, \beta_2, \ldots$ are constants. Since the formula with a large number of constants is of little practical use, Graetz neglected the constants $\beta_1, \beta_2, \ldots$ which are of small magnitude and thus obtained

$$\eta = a\frac{\vartheta_0 - \vartheta}{\theta},$$

or if the temperatures are changed to the absolute scale,

$$\eta = a\frac{T_{cr} - T}{T - T_s} \tag{44}$$

9

where T_{cr} is the critical temperature and T_s is the temperature of solidification.

Applying this formula to the data of Rellstab, and Pribram and Handl, Graetz found that it was satisfactory in some fifty cases, but it is inapplicable to the fatty alcohols.

This formula is a particular form of the one already given by Slotte. Slotte (1883–90) reached the conclusion that none of the preceding formulas gives satisfactory results with substances whose viscosity changes rapidly with the temperature, as is generally true of very viscous substances. He proposed the formula

$$\eta = \frac{a}{(b + T_o)^n} \tag{45}$$

where T is the temperature centigrade and a, b, and n are arbitrary constants. Slotte found that this formula gave better results than any other and Thorpe and Rodger adopted it in their great work as the most satisfactory formula at their disposal, but this formula like the others breaks down when applied to the alcohols. In the case of several of the alcohols it was necessary to apply the formula three times with different constants over different parts of the curves in order to reproduce the observed values with anything like the desired accuracy. The values of n vary from 1.4 to 4.3.

Several exponential formulas have been proposed. Reynolds (1886) and Stoel (1891) suggested the formula

$$\eta = ae^{-\gamma T_o} \tag{46}$$

which Reynolds found to apply to olive oil and Stoel and De Haas (1894) found to apply to methyl chloride between the boiling-point and the critical temperature. In this formula e is the natural logarithmic base and a and γ are constants. Heydweiller in 1895 investigated benzene and ethyl ether over a similar range of temperature, and found that the formula holds between the reduced temperatures of 0.62 and 0.87 for the purposes of interpolation; but that similar systematic deviations occur for all substances, which is due to the fact that the temperature coefficient of the viscosity is not constant but passes through a point of inflection. Below the boiling-point the viscosity-temperature curve is convex toward the temperature axis while near the

critical temperature it is concave, and the deviations from the formula are considerable. Heydweiller made the interesting observation that within the series of compounds with which he worked the temperatures of equal viscosity are in the ratio of their critical temperatures. But to this rule water and the alcohols are exceptional.

De Heen in his *Theorie des Liquides* (1888) found the following formula satisfactory

$$\eta = \eta_0(1 + ae^{-bT_c})^c \tag{47}$$

The constant c varies little from liquid to liquid from 2.65 to 2.85.

Jaeger (1893) has worked out a kinetic theory of liquids on the ground that the transfer of momentum takes place by the molecules passing back and forth from one layer of molecules to another. He gives the expression

$$\eta = \frac{2r^2\rho v}{3\lambda} \tag{48}$$

where r is the radius of a molecule, v its mean velocity, λ its mean free path, and ρ is the density of the liquid.

Similarly Kamerling Onnes has derived a formula from the theory of corresponding condition of van der Waals,

$$\frac{\eta V^{\frac{2}{3}}}{\sqrt{MT_{cr}}} = \text{Constant} \tag{49}$$

where V is the molecular volume, M the molecular weight, T_{cr} the critical temperature, and $\eta V^{\frac{2}{3}}$ is the molecular surface friction. The formula does not apply at low temperatures and perhaps only perfectly as the critical temperature is reached.

Perry (1893) states that sperm oil cannot be represented by any single formula since a discontinuity occurs in the viscosity and density curves at 40°. It should be added that he took care that the velocity of flow did not exceed the critical value for viscous flow. He employed two sets of constants in the formula

$$\eta = a(T - b)^{-c} \tag{50}$$

Examining a considerable number of the formulas which had already proved of value and given above, Duff (1896) obtained the following formula by integrating the curve of subtangents derived from them:

$$\eta = C\left(\frac{T + a}{T + \beta}\right)^n \tag{51}$$

This formula reproduces observed values of all classes of compounds with remarkable fidelity, but it contains four constants.

Finally Batschinski (1901) has indicated that the viscosity varies inversely as the cube of the absolute temperature

$$\eta = \frac{E}{T^3} \tag{52}$$

where E is dependent upon the nature of the liquid and is called "the viscosity parameter." Using the data of Thorpe and Rodger, Pribram and Handl, Gartenmeister and others, Batschinski has tested his expression fully. While it gives very good
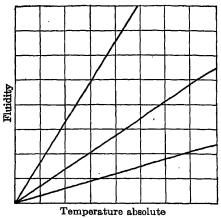
Fig. 48.—Diagram illustrating ideal fluidity-temperature curves.
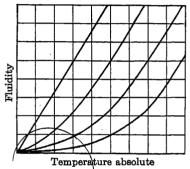
agreement in many cases, there are numerous exceptions, particularly water, the alcohols, acids and anhydrides (*cf.* Eq. (41) for mercury).

Fluidity and Temperature.—From the evidence given in Chapter I to prove that fluidities are normally additive in homogeneous mixtures, it would appear probable that fluidity-temperature curves in their simplest form are straight lines, and since every liquid is theoretically capable of existing in an undercooled condition, these curves meet at absolute zero. The equation for the fluidity-temperature curves of all substances should be

$$\varphi = aT$$

which is the same as Eq. (43). A family of curves would present the appearance shown diagrammatically in Fig. 48.

Unfortunately, fluidity-temperature curves are not generally linear throughout. Even the aliphatic hydrocarbons, which are supposedly unassociated, give curves which depart considerably from linearity. For this peculiarity two possible explanations suggest themselves. The effect of expansion is not linear except in the case of mercury and there may be changes in the molecular weight, either association or dissociation. Later each of these causes will be considered in detail. Suffice it for the present to note that the alcohols, Fig. 46, give fluidity-temperature curves which are strongly curved at low fluidities, but the curves tend to become linear at high fluidities as is true of the other classes of compounds. In a given homologous series the evidence at hand shows a tendency for the fluidity-temperature curves near the ordinary boiling-points to become parallel to each other with equal distances between them. But they must all meet at absolute zero of temperature, which requires that in the higher members of the series at least there should be a region of rapid curvature. This is the

Fig. 49.—Diagram illustrating the fluidity-temperature curves of a "homologous series" of liquids.

region of "softening" which has been observed in many viscous substances. According to the views here presented the phenomenon of softening may not occur in any substance consisting of monatomic molecules but will certainly become manifest as we increase the complexity of the molecule. These ideas are represented diagrammatically in Fig. 49. If they represent accurately the actual behavior of substances, the fluidity-temperature curves have the following properties: (1) They all approach linearity as the fluidity increases, *i.e.*, each tends to become asymptotic to a line which forms an acute angle with the temperature-axis. (2) As the fluidity becomes very small, each curve tends to become asymptotic to the temperature-axis itself. Thus the general form of the fluidity-temperature curve must be a hyperbola, since this is the

curve which contains these properties. The linear curve for
substances like mercury is of course but a special and extreme
case. It is very important that we find out whether other mon-
atomic liquids, such as, for example, liquid sodium, argon, *et cet.*
have a linear volume temperature and fluidity-temperature curve.
. Given the properties of a general fluidity-temperature curve
it is easy to obtain the curve which contains these properties.
The simplest is

$$T = A\varphi + C - \frac{B}{\varphi} \tag{53}$$

For the simplest case, which we have in mercury, the constants
B and C are each zero and our equation becomes that of Batschin-
ski (41); for other substances at high temperatures the term B/φ
becomes negligible and the equation becomes that of the asymp-
tote

$$T = A\varphi + C$$

This linear equation can be transformed into the formula of
Meyer and Rosencranz. Thus while our formula (51) agrees
with some of the simpler formulas which have been proposed,
it is at variance with those which have had the widest usefulness.
For example, the Meyer-Poiseuille formula may be written

$$\varphi = A + BT_c + CT_c^2 \tag{53a}$$

which is the equation of a parabola. Were it valid as a general
equation, the fluidity would have a minimum value at 0°C,
and at high temperatures the fluidity curve would tend to be-
come parallel to the fluidity-axis. It needs no argument to show
that this equation cannot be general.

By increasing the number of terms, the formula of Meyer-
Poiseuille becomes the second formula of Slotte,

$$\varphi = A(B + T_c)^n$$

The effect of the additional terms is to increase the curvature
but it does not remedy the defects noted. The equation of
Stoel and others may be regarded as a special case of Slotte's
equation where the number of terms is infinite.

The formula of Graetz is defective in that it assumes that the
fluidity becomes zero at a definite positive temperature and that
at the critical temperature the fluidity is infinite. Neither of
these assumptions can longer be held.

TABLE XXXIV.—THE CONSTANTS IN THE EQUATION $T = A\varphi + C - \dfrac{B}{\varphi}$

	Substance	A	B	C	Mean per cent difference
1	Water.....................	0.27727	1,263.3	278.80	0.17
2	Bromine...................	0.79098	1,376.3	227.16	0.03
3	Nitrogen peroxide...........	0.32274	3,837.6	231.92	0.00
4	Pentane...................	0.16544	14,937.0	256.61	0.03
5	Isopentane................	0.18327	10,454.0	234.17	0.03
6	Hexane....................	0.21892	9,137.8	254.03	0.04
7	Isohexane.................	0.20708	9,562.8	252.85	0.05
8	Heptane...................	0.23203	8,681.2	272.70	0.09
9	Isoheptane................	0.22445	869.84	267.35	0.12
10	Octane....................	0.27055	6,332.6	277.25	0.16
11	Trimethyl ethylene..........	0.21942	6,770.3	203.56	0.06
12	Isoprene..................	0.21505	7,126.5	208.74	0.09
13	Diallyl...................	0.19818	9,774.4	247.75	0.06
14	Methyl iodide..............	0.44916	3,107.1	215.85	0.01
15	Ethyl iodide...............	0.43828	4,348.2	243.29	0.04
16	Propyl iodide..............	0.46571	3,474.4	255.85	0.11
17	Isopropyl iodide...........	0.41279	4,108.8	262.07	0.14
18	Isobutyl iodide............	0.46881	2,727.2	264.30	0.23
19	Allyl iodide...............	0.47443	2,994.0	249.80	0.11
20	Ethyl bromide.............	0.35853	4,073.2	217.39	0.02
21	Propyl bromide.............	0.36084	4,950.6	248.95	0.04
22	Isopropyl bromide...........	0.33069	5,009.9	248.57	0.03
23	Isobutyl bromide...........	0.34098	4,754.4	270.75	0.20
24	Allyl bromide..............	0.36448	4,467.7	241.77	0.06
25	Ethylene bromide...........	0.68897	1,421.6	277.92	0.23
26	Propylene bromide..........	0.64567	1,463.0	278.53	0.34
27	Isobutylene bromide.........	0.65358	1,060.2	288.40	0.04
28	Acetylene bromide...........	0.63374	2,275.3	249.46	0.12
29	Propyl chloride.............	0.25540	7,465.2	246.74	0.05
30	Isopropyl chloride...........	0.24993	5,881.9	234.22	0.01
31	Isobutyl chloride...........	0.28656	4,973.0	253.00	0.02
32	Allyl chloride..............	0.26292	6,377.2	234.10	0.03
33	Methylene chloride..........	0.39803	2,666.5	212.97	0.04
34	Ethylene chloride..........	0.44121	2,219.3	258.83	0.08
35	Ethylidene chloride.........	0.33277	4,651.6	247.99	0.04
36	Chloroform.................	0.40697	4,400.0	245.73	0.07
37	Carbon tetrachloride.........	0.47337	1,807.5	262.15	0.08
38	Carbon dichloride..........	0.55768	3,081.6	259.13	0.20
39	Carbon disulfide	0.26901	16,751.0	282.23	0.17
40	Methylsulfide..............	0.25514	8,387.6	230.57	0.01
41	Ethylsulfide...............	0.28517	6,447.9	258.00	0.11
42	Thiophene.................	0.38204	2,967.2	254.95	0.09
43	Dimethylketone.............	0.23871	8,905.0	247.64	0.03
44	Methylethylketone..........	0.27275	5,572.6	252.32	0.08
45	Diethylketone.............	0.28145	6,179.3	262.41	0.16
46	Methylpropylketone.........	0.29251	5,544.3	263.21	0.15
47	Acetaldehyde..............	0.15205	18,364.0	265.13	0.006
48	Formic acid................	0.52465	963.4	281.57	0.19

TABLE XXXIV.—(*Continued*)

Substance	A	B	C	Mean per cent difference
49	Acetic acid................	0.42437	2,716.8	291.81	0.22
50	Propionic acid.............	0.43533	2,908.9	287.53	0.41
51	Butyric acid...............	0.45359	1,951.9	296.43	0.69
52	Isobutyric acid............	0.45841	2,143.6	288.41	0.43
53	Acetic acid anhydride.......	0.40620	2,747.8	273.61	0.31
54	Propionic acid anhydride....	0.39705	2,444.6	287.45	0.61
55	Diethy ether...............	0.16574	14,674.0	256.72	0.07
56	Benzene...................	0.32052	2,633.1	260.82	0.05
57	Toluene...................	0.32688	4,193.5	262.66	0.12
58	Ethyl benzene.............	0.34180	4,540.8	273.54	
59	Ortho xylene..............	0.37738	3,009.3	271.96	0.28
60	Meta xylene...............	0.34134	4,542.9	266.82	0.19
61	Para xylene...............	0.32087	5,127.4	277.17	0.20
62	Methyl alcohol............	0.24316	4,498.9	279.01	0.14
63	Ethyl alcohol.............	0.28395	2,398.6	298.39	0.12
64	Propyl alcohol............	0.31496	1,211.7	308.41	0.35
65	Isopropyl alcohol.........	0.29810	738.16	300.17	0.36
66	Butyl alcohol.............	0.33610	877.08	311.94	0.72
67	Isobutyl alcohol..........	0.33648	512.18	309.72	0.81
68	Trimethyl carbinol........	0.29657	260.86	305.73	0.33
69	Amyl alcohol, active......	0.35020	376.48	311.50	1.17
70	Amyl alcohol, inactive....	0.36060	513.18	312.40	1.08
71	Dimethyl ethyl carbinol....	0.29578	259.87	307.20	0.87
72	Allyl alcohol.............	0.28815	1,935.7	299.53	0.23
73	Methyl formate...........	0.34444	1,292.0	198.31	0.01
74	Ethyl formate............	0.29418	4,858.1	239.32	0.02
75	Propyl formate...........	0.29797	4,800.6	260.44	0.06
76	Methyl acetate...........	0.26047	6,475.7	249.48	0.03
77	Ethyl acetate............	0.27056	5,361.2	257.20	0.06
78	Propyl acetate...........	0.29534	4,262.6	267.50	0.15
79	Methyl propionate........	0.27300	5,954.3	261.08	0.15
80	Ethyl propionate.........	0.29125	4,846.4	264.51	0.12
81	Methyl butyrate..........	0.30210	4,315.3	265.89	0.15
82	Methyl isobutyrate.......	0.28615	5,073.2	264.44	0.15
83	Methyl propyl ether......	0.21797	7,206.3	224.27	0.08
84	Ethyl propyl ether.......	0.20872	8,933.6	255.80	0.05
85	Dipropyl ether...........	0.23579	6,858.5	266.34	0.14
86	Methyl isobutyl ether.....	0.21201	8,748.8	250.76	0.03
87	Ethyl isobuty ether.......	0.22545	7,188.2	260.96	0.09

We will now see how far the fluidity Eq. (53) can be used to reproduce the experimentally observed values. In Table XXXIV we give the constants for the 87 substances investigated by Thorpe and Rodger and in the last column of the table we give the average percentage difference between the observed and calculated values.

The mean percentage difference between the calculated and

observed values is 0.17 for the 87 substances and based on some 1,000 duplicate observations. If we omit the alcohols, this difference falls to 0.09 for 70 substances. This is much better agreement than Thorpe and Rodger obtained with Slotte's equation, since the percentage difference is nearly twice the above, *viz.*, 0.15 per cent for 64 substances. But the real test is with substances which give fluidity curves departing widely from the linear type and here Slotte's equation breaks down completely.

For this type of substances, the fluidity Eq. (53) with three constants does not reproduce the observed values to the limit of experimental error, but a great improvement can be made by introducing another constant and writing the equation

$$T = A\varphi + C - \frac{B}{\varphi + D} \tag{54}$$

For example, the mean divergence between the observed and calculated values for the eight substances, which gave the largest percentage difference, was 0.77 per cent with the simpler formula; the Eq. (54) with four constants reduces this to only 0.07 per cent which is nearly within the limits of the experimental error. In the case of water, which gave a mean difference of only 0.17 per cent with the simpler formula, the difference is reduced to 0.01 per cent and similarly in the case of octane it is reduced from 0.16 to 0.02 per cent. For reference, the constants for these substances are given in Table XXXV.

TABLE XXXV.—THE CONSTANTS IN THE EQUATION $T = A\varphi + C - \dfrac{B}{\varphi + D}$

Substance	A	B	C	D	Mean per cent difference
Water.....................	0.23275	8,676.8	309.17	120	0.01
Octane....................	0.14507	100,745.0	438.10	400	0.02
Butyric acid...............	0.16154	70,630.0	504.44	250	0.02
Isobutyric acid.............	0.23862	43,665.0	433.17	200	0.06
Propionic acid anhydride.....	0.23619	52,294.0	425.82	250	0.07
Butyl alcohol...............	0.23695	4,802.0	349.71	40	0.04
Isobutyl alcohol............	0.23700	2,993.7	340.66	30	0.09
Active amyl alcohol.........	0.24650	2,942.8	346.82	30	0.08
Inactive amyl alcohol.......	0.24191	3,908.7	354.17	35	0.09
Dimethyl ethyl carbinol......	0.22988	2,124.0	328.84	30	0.09

Fluidity and Pressure.—To find the effect of pressure on viscosity, Coulomb in 1800 measured the rate of oscillation of a disk in a liquid both under atmospheric pressure and when the space above the liquid had been evacuated. It was found that the viscosity is independent of small changes of pressure. This conclusion was confirmed by Poiseuille in 1846, using his transpiration method.

However, quite the opposite conclusions must be drawn from the experiments of Warburg and Babo (1882), but they employed liquid carbon dioxide at 25.1°C, which is quite near the critical temperature, and they used pressures from 70 to 105 atmospheres. It is worth noting that under these conditions the compressibility of carbon dioxide is 0.00314 which is about 18 times as great as that of ether at the same temperature. They found an increase in the viscosity which amounted to over 25 per cent, and it therefore seemed possible that the effect was caused by the change in density and that a similar effect would be observed in other liquids if high enough pressures were employed.

Warburg and Sachs (1884) continued the previous investigation and indeed found that liquid carbon dioxide, ether, and benzene all suffer an increase in viscosity on increasing the pressure, but they also noted that water is exceptional in that an increase in pressure actually lowers the viscosity. They sought to connect the viscosity and pressure by means of the following linear formula,

$$\eta = \eta_0(1 + Ap). \qquad (55)$$
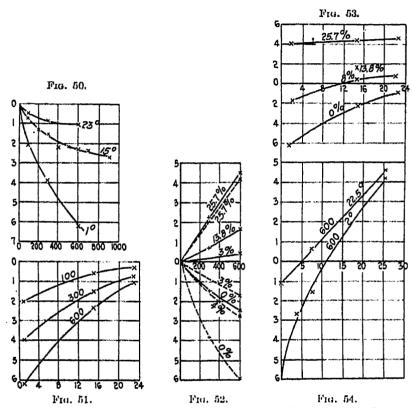
The values of the constant A are given in Table XXXVI.

TABLE XXXVI.—CONSTANTS IN EQUATION (53)

Substance	Carbon dioxide	Ether	Benzene	Water
Temperature of experiment.........	25.1	20	20	20
Critical temperature...............	30.9	190	280.6	365
$A \times 10^6$........................	7,470	730	930	−170

The striking fact that water is peculiar in this as in so many other respects was discovered independently by Röntgen (1884). It was made the subject of a special study by Cohen in 1892,

working at 1, 5, and 23° at pressures ranging from 1 to 600 atmospheres and using pure water and four solutions of sodium chloride of different concentrations. The nature of his results is shown in Figs. 50 to 54. In Fig. 50 the percentage change in the time of flow, $[(t_1 - t_p)/t_1]100$, is plotted as ordinates

Fig. 53.

Fig. 50.

Fig. 51.   Fig. 52.   Fig. 54.

The effect of pressure on the viscosity of aqueous solutions.   (*After Cohen.*)

against the pressures as abscissas. It is observed that the viscosity continues to decrease for all pressures up to 900 atmospheres, but the decrease becomes very slight at 23°.   In Fig. 51 the ordinates are the same as before but the temperatures are plotted as abscissas. It is evident that the curves are approaching each other and the zero axis, and thus they indicate the possibility that at some higher temperature the curves will cross

the zero axis and the viscosity will then increase with the pressure as in other liquids.

In Fig. 52 the percentage change in the time of flow is plotted against the pressure as in Fig. 50. A saturated solution (25.7 per cent) is seen to behave unlike pure water but like other liquids in that the pressure causes an increase in the time of flow. The curves for other concentrations lie between those for pure water (0 per cent) and those for the saturated solution. The continuous curves represent measurements at 14.5° and the dotted curves represent measurements at 2°. From a comparison of these it is evident that the temperature coefficient of the percentage change in the time of flow decreases rapidly as the concentration of the solution is increased. This is shown more clearly in Fig. 53 where the temperatures are plotted as abscissas against the percentage change in the time of flow for a pressure of 600 atmospheres, *i.e.*, the percentage change in the time of flow is nearly constant in the most concentrated solution. Furthermore in an 8 per cent solution at a pressure of 600 atmospheres, the effect of pressure on the time of flow is zero at 11°. Below that temperature, pressure decreases the time of flow; above that temperature, it increases it.

The relation of the percentage change in the time of flow at 600 atmospheres pressure as ordinates to the percentage concentration as abscissas is indicated in Fig. 54. At 22.5° the percentage change of the time of flow is a linear function of the concentration, but at 2° this is no longer true, the effect of the first additions of the salt to water being much greater than subsequent additions. The curves do not cross, hence the effect of pressure in the concentrated salt solutions is greatest at the high temperatures even up to the point of saturation. Cohen found the opposite to be true of turpentine, *viz.*, the effect of pressure is greatest at low temperatures. According to Warburg and Sachs, ether behaves like turpentine and benzene like sodium chloride solutions.

Hauser (1901) found that the effect of pressure upon the viscosity of water continually decreases as the temperature is raised until it becomes zero at 32° up to 400 atmospheres. Above this temperature the viscosity increases with the pressure as in other liquids, and the effect becomes more pronounced as the

temperature is raised, amounting to 4 per cent for a pressure of 400 atmospheres at 100°.

Faust (1913), using pressures as high as 3,000 kg per square centimeter, found that the viscosity of ether, alcohol, and carbon disulfide were each increased by about fourfold. This result has important bearing upon the theory and practice of lubrication. And very recently J. H. Hyde (1920) has reported to the Lubricants and Lubrication Committee of the Department of Scientific and Industrial Research the results of an investigation of the viscosity of a variety of lubricating oils, using pressures up to 7 tons per square inch. He made the important deduction that the mineral oils increase in viscosity far faster with the pressure than do the fixed oils. Thus the viscosity of Mobiloil BB increases over twenty-six-fold, whereas with the same increase in pressure the fixed oils increase in viscosity about fourfold.

Fluidity and Volume.—We have now before us the two following generalizations: (1) An increase in pressure is usually associated with a decrease in fluidity, and (2) an increase in temperature is usually associated with an increase in fluidity. To be sure, there are prominent exceptions to both generalizations, as, for example, water, in its behavior under pressure and sulfur, as affected by temperature. But water and sulfur are highly associated in the liquid state so that an explanation of these exceptions is possible on the basis of changing molecular weights.

Lowering of pressure or raising of the temperature of a liquid have one thing in common in addition to their similar effect upon the fluidity—they both produce an increase in the volume, to which there are very few exceptions. It is worth while therefore to investigate the question of how much of the change in fluidity can be attributed primarily to a change in volume. If one has in mind the fact that in gases, where the volume changes are large, the fluidity is nearly independent of the volume, one would naturally expect the changes in the volume of liquids to be responsible for only a small part of the fluctuations in fluidity which actually exist. But the viscosities of gases and liquids arise from entirely different causes, hence reasoning by analogy is useless.

The parallelism between fluidity and volume may be followed

in another direction, for generally speaking whenever two liquids are mixed and a contraction takes place, there seems to follow a decrease in fluidity. Alcohol and water, acetic acid and water, and chloroform and ether are a few examples. On the contrary, when liquids mix with an expansion in volume, the mixture has a greater fluidity than we would expect from the linear fluidity-volume concentration curve. Methyl iodide and carbon disulphide furnish an example of this sort (Bingham *et al.*, 1913). The above facts have suggested to various workers (Brillouin (1907), Part 2, p. 127; Dunstan and Thole (1909), p. 204; Bingham (1911), p. 270) that fluidity and volume are intimately related, more so in fact than fluidity is to either temperature or pressure.

In spite of this intimate relationship, it has been little investigated. Slotte (1894) stated that the logarithms of the viscosity are proportional to the logarithms of the specific volume, and from this observation he deduced his second Eq. (43). But the most important discovery was made by Batschinski in 1913. He found that the relation between the molecular volume V and the fluidity may be expressed in the following formula:

$$\phi = C(V - \Omega) \tag{56}$$

where Ω and C are constants. The constant Ω may be defined as the limiting value which the molecular volume of any liquid can have as its fluidity approaches zero, and it is therefore called the "molecular limiting volume." Consequently the difference $V - \Omega$ may be called the "molecular free volume" and the above relation may be very simply expressed as follows: *The fluidity varies directly as the free molecular volume.* Sixty-six of the 87 substances investigated by Thorpe and Rodger exhibit this relationship and the values of the fluidity, as calculated from the volume, seldom deviate from the observed values by more than 1 per cent. The 21 substances for which the agreement is not good include the alcohols, water, some of the acids, the acid anhydrides, and some of the halides. These substances are generally regarded as associated and it may well be that the molecular weight is not constant as the temperature is raised. The nature of the very remarkable agreement obtained is shown in Table XXXVII containing data for benzene obtained by Thorpe and Rodger between 0° and the boiling-point and by Heydweiller

from the boiling-point up to 185.7°. This agreement is shown graphically for a number of substances in Fig. 55.

TABLE XXXVII.—CALCULATION OF THE FLUIDITY OF BENZENE FROM ITS VOLUME BY MEANS OF THE FORMULA $\varphi = (V - 81.76)/0.045,35$

Temperature	φ Observed	Specific volume	φ Calculated	Difference
0.0	110.8	1.1124	111	0
10.0	131.5	1.1242	132	0
20.0	154.1	1.1377	155	1
30.0	178.0	1.1514	179	1
40.0	203.1	1.1661	204	1
50.0	228.8	1.1812	230	1
60.0	256.1	1.1966	256	0
70.0	284.9	1.2124	283	−2
80.0	305.8	1.2278	311	5
78.4	314.0	1.2253	310	−4
100.5	383.7	1.2624	385	1
131.8	504.8	1.3255	510	5
161.4	646.8	1.3957	649	2
185.7	797.4	1.4661	794	−3

Batschinski tested his formula with the recently obtained data of Phillips (1912) on the viscosity of carbon dioxide under varying pressures. He thus proved that at least while the substance remains liquid the fluidity varies directly as the free volume.

TABLE XXXVIII.—CALCULATION OF THE FLUIDITY OF CARBON DIOXIDE FROM ITS VOLUME BY MEANS OF THE FORMULA $\varphi = \dfrac{V - 33.2}{0.0169}$

Pressure, atmospheres	Observed	Specific volume	Calculated	Per cent. difference
110.5	1,299	1.259	1,300	0
96.0	1,443	1.316	1,450	1
82.0	1,689	1.397	1,640	−3
76.0	1,890	1.471	1,850	−2
72.0	2,183	1.575	2,080	−5

If we could always compare the fluidities of liquids at a definite multiple of the molecular limiting volume, it is evident that the effect of the volume, and therefore of temperature and pressure in so far as they affect the volume, would be eliminated. Such a procedure would enormously simplify fluidity relationships. As a matter of fact Batschinski has shown that the molecular limiting volume possesses an additive character, the values of
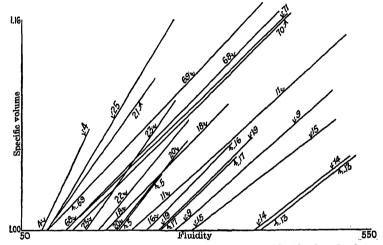
Fig. 55.—Relative volume-fluidity curves after Batschinski using the data of Thorpe and Rodger.

4, Bromine; 5, nitrogen peroxide; 9, isohexane; 11, isoheptane; 13, trimethylethylene; 14, isoprene; 15, diallyl; 16, propylchloride; 17, isopropylchloride; 18, isobutylchloride; 19, allylchloride; 20, methylenechloride; 21, ethylenechloride; 22, ethylidenechloride; 23, chloroform; 25, perchlorethylene; 68, ethylbenzene; 69, orthoxylene; 70, metaxylene; 71, paraxylene.

the atomic constants being H = 4.3, O = 8.6, C = 8.8, Cl = 19.2, Br = 24.8, I = 32.0, S = 19.0, a double bond = 3.3, and an iso-grouping = 0.7. For 53 of the substances studied by Thorpe and Rodger the differences between the observed and calculated values of the molecular limiting volume do not exceed 2 per cent. The limiting specific volume is approximately 0.307 of the critical volume which is close to the parameter b of van der Waals' equation.

We are now in a position to get a very clear understanding of the law that the fluidity is proportional to the free volume.

When the molecules of a liquid are closely packed, the volume reaches its minimum value and the fluidity is zero. With tetrahedral close-packing of the molecules, shear would require rupture of the molecules themselves. If there are pore spaces between or within the molecules, they do not give rise to fluidity, so that the molecules somewhat resemble close-fitting solid figures. As the fluid expands, due to molecular agitation, the volume of the molecules themselves, *i.e.*, the inner molecular volume may remain the same, but the ordinary, *i.e.*, the outer molecular volume increases. The law states that the fluidity originates solely in the free space which is the difference between the outer molecular volume, or the volume *occupied* by the molecules, and the inner molecular volume or the space *filled* by the molecules in the sense indicated above. Given two substances with the same outer molecular volume, it is evident that the one with the larger molecular kernel will have the smaller fluidity. It is therefore natural to expect that the limiting molecular volumes should be additive as Batschinski has found to be the case. This opens the way to a study of the relation between fluidity and chemical composition and constitution which is most fascinating. It is very simple to measure the outer molecular volume, and if this with the fluidity will give a certain and easy method for determining the inner molecular volume, it is a result much to be desired. It is apparent that density and fluidity determinations should go hand in hand.

If the above reasoning held true for gases as well as liquids, the fluidity isothermals of carbon dioxide should closely resemble the familiar volume isothermals. By substituting for the volume its value in terms of the fluidity given by Batschinski's law, we would obtain a modified van der Waals' equation. As a matter of fact van der Waals' equation may be written

$$T = \frac{P}{R}v - \frac{pb}{R} - \frac{a}{Rv} + \frac{ab}{Rv^2}$$

but since viscosities are ordinarily measured at constant, *i.e.*, atmospheric pressure, this may be written

$$T = A\varphi + C - \frac{B}{\varphi + D} + \frac{E}{(\varphi + D)^2}$$

where A, B, C, D and E are constants. This is identical with Eq. (54) which is entirely satisfactory for liquids, except that it

10

contains an additional term, which becomes negligible when the fluidity is large.

That the fluidity isothermals of carbon dioxide do not in any way resemble the volume isothermals as we pass into the gaseous
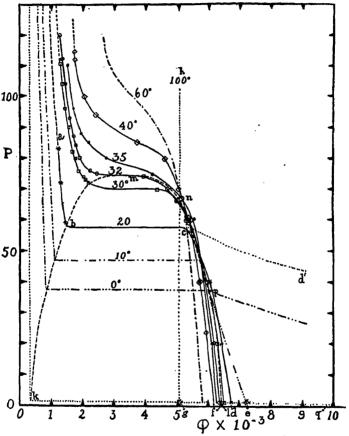
FIG. 56.—The fluidity isothermals of carbon dioxide based on the measurements of Phillips.

condition is sufficiently obvious from inspection of Fig. 56, plotted from Phillips' data. The continuous curves are drawn between observed points. The broken lines are added for diagrammatic purposes. The left half of the figure, corresponding to low fluidity and temperature, presents a strong similarity

to the familiar pressure-volume diagram. At the highest pressures, the fluidity is not greatly affected by a change in pressure, *e.g.*, at 32° and a pressure of 120 atmospheres, a lowering of the pressure by 4 atmospheres causes an increase in fluidity of less than 4 per cent. At a lower pressure the fluidity becomes extremely susceptible to changes in pressure, a lowering of the pressure by 4 atmospheres at 76 atmospheres causing an increase in the fluidity of a full 100 per cent at 32°. The gaseous and liquid phases are both present inside of the curve *kbmcl*. But the right side of the figure is entirely different from the familiar pressure-volume diagram. Instead of the fluidity being highly susceptible to changes in pressure, as is the volume, it is but slightly affected, *e.g.*, at 32° and 50 atmospheres pressure, a lowering of the pressure by 4 atmospheres causes only a 10 per cent increase in the fluidity.

Let us follow in detail the isothermal of carbon dioxide at 20° which is well below the critical temperature. At high pressures, the fluidity increases nearly linearly from *a* to *b*; there is then a sudden increase in the fluidity from 1,500 to 5,300 absolute units, as the substance passes from the liquid to the gaseous condition. We should expect the fluidity to continue to increase as the pressure is further lowered, giving the curve *cd'*, but the curve actually obtained is *cd*. We have seen that the fluidity of liquids increases with the temperature, while, on the other hand, the fluidity of gases decreases with the temperature, hence, the pressure-fluidity curves for different temperatures must intersect each other. The figure proves that not only is this true, but, when the temperatures are sufficiently high, the curves all tend to pass through the particular point *n*, so that at this point the fluidity is independent of the temperature; for the lower temperatures, the curves seem to intersect each other on the curve *ncl*.

Collisional and Diffusional Viscosity.—That the pressure-fluidity curves do not follow an equation of the van der Waals type as the fluidity becomes large may be due to the appearance of a new type of viscous resistance. We must therefore now investigate more particularly into the nature of viscous resistance. One's first impulse in looking for a cause of viscosity is to assume a cohesion between the particles which is exerted during motion and acts in opposition to motion,[1] but with the develop-

[1] "Kinetic Theory of Gases," MEYER, p. 171.

ment of the kinetic theory of gases, it became evident that
viscous resistance arises from the diffusion of the particles
of high translational velocity into layers whose translational
velocity is lower, and *vice versa*. According to this explanation,
the loss of translational velocity must increase with the tempera-
ture, which accords with the fact that the fluidity of a gas
decreases as the temperature is raised.

But in liquids the fluidity *increases* with the temperature
and it is generally agreed that there is a second cause of viscous
resistance, which, without any very good reason in its favor,
has been repeatedly attributed to the attraction between the
molecules. According to Batschinski[1] "If we think of two parallel
layers of liquid as of two rows of men, the men moving in place
of molecules, we must assume that these men take hold of their
nearest neighbors and hold them for a time." This explanation is
however inadequate, for a particle A, coming within the range
of attraction of a particle B in an adjacent layer supposed to be
possessed of slightly less translational velocity, will be accel-
erated and only after passing B will the retardation take place.
Apparently the two actions exactly neutralize each other, or if
they do not there must result a destruction of energy in violation
of the first law of thermodynamics. No reasonable hypothesis
has been proposed to extricate us from this dilemma, on the
basis of cohesion, hence, we are forced to look for some other
cause. Whatever the explanation, it must show how transla-
tional or ordered motion is being continuously transformed
into heat or disordered motion.

To get a clearer idea of the nature of the two causes of viscous
resistance, we imagine two parallel planes A and B, the former
moving to the right parallel to itself in respect to the second
plane, which for convenience only may be assumed to be at rest.
We will first assume that between the planes there is a highly
rarefied gas. If the walls are smooth and unyielding and the
particles of gas perfectly elastic spheres, we will not have a
model of viscous flow; for as the particles collide with the sur-
faces, the angle of rebound will be equal to the angle of incidence,
there will be no translational velocity transmitted to or from the
walls and the so-called "slipping" would be perfect. In order

[1] (1913) p. 643.

to obtain a model of viscous flow it is therefore necessary to assume that the surfaces are not perfectly smooth. In view of the known discontinuity of matter, one could hardly assume a smooth surface, and the least degree of roughness which one could well assume would be one made up of equal spheres whose centers lie in the same plane and as closely packed together as possible. That there is a greater degree of roughness in all ordinary surfaces is probable, but it suffices for our present purposes to show in what follows that this simple assumption in regard to the nature of the surfaces gives a workable model of viscous flow.

It becomes necessary to show that momentum is being con-
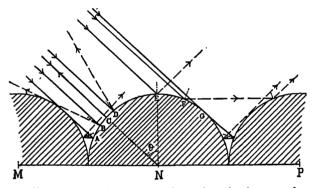
Fig. 57.—A diagram illustrating how translational motion becomes changed into vibrational motion by striking a rough surface.

tinually taken from the surface *A* and changed into heat. That the model meets the requirements depends upon the truth of the following theorem: *When a series of elastic particles strike a rough surface, the resultant component of velocity along the surface will be diminished.* Let *M*, *N*, and *P* in Fig. 57 represent the section through the centers of three of the greatly magnified spheres supposed to make up the surface. It is evident that if a small particle were to strike such a surface at an angle *θ*, its possible paths in striking the sphere *N* would all lie between *A* and *G*. Considering the directions of the particle before and after collision, assuming that the angle of rebound at any point of the surface is equal to the angle of incidence, we find that for possible paths between *B* and *D* the average resultant velocity on

rebound is exactly opposite in direction, although diminished in amount. For paths between A and B a particle would collide with M on rebounding from N but the component of the velocity in the direction NP is diminished. Also for paths between D and E, as well as between F and G, the component of the velocity in the direction NP will be diminished. Only between E and F is the component in the direction of the flow greater after collision than before. But the distance EF becomes zero when $\theta = 90°$ and it has its maximum value when $\theta = 0°$, *i.e.*, when the translational motion is zero. Since all of the paths between A and G are equally likely, it is clear that for this section at least the average translational velocity is diminished by collision, irrespective of the size of the angle or of the velocity of the particle, and the same would be true even if the particle were of considerable size. The same must be true *a fortiori* for sections other than the one passing through the centers of the spheres, for then there must, after collision, be a component velocity at right angles to the plane of the paper and therefore to the direction of flow. The section would be similar to the one given except that the circles would not touch, the spaces between them corresponding to the pores of the surface in which the translational velocity would quite certainly be changed to disordered motion.

It follows from the above that a fluid in contact with a rough surface tends to have a translational velocity identical with that of the surface[1]. Reverting to our model, the theorem explains how molecules striking the surface A receive its translational velocity and how this translational velocity becomes transformed into disordered motion at the surface B. If the motion of the surface A were suddenly stopped, all of the flow would cease in a time which, for gases made up of particles whose velocity is expressed in kilometers per minute, must be quite inappreciable. It is to be particularly noted that collisions between molecules of a gas are unnecessary for this type of viscous resistance. This type of resistance is caused solely by the diffusion of the molecules and it therefore may be appropriately referred to as **diffusional viscosity.**

For the opposite extreme we may take for consideration a very viscous liquid. The molecular free path is so greatly reduced

[1] *Cf.* Jeans (1904) and Dushman (1921).

that diffusion between adjacent layers is comparatively slight, whereas the volume of the molecules themselves is a considerable portion of the total volume of the liquid. Given a layer of molecules C whose translational velocity is higher than that of another layer D, there must of necessity occur collisions between the two layers due to the flow, and quite irrespective of any diffusion, provided only that the diameter of the molecules is greater than the distance between the layers. On collision the translational velocity is partly communicated to the slower moving molecules of the layer D, so that the molecules of the layer D have a mean resultant velocity in the direction of the flow, the remainder of the translational motion being converted into disordered motion or heat. When the system has reached a steady state, any layer D imparts to the layer E below it the same amount of translational momentum that it has received from the layer C above it, except for the amount of energy which is being continuously changed into heat, and it is this disappearance of translational momentum which gives rise to the new type of viscous resistance known as **collisional viscosity**. Since each layer is able to transmit but a portion of the translational momentum which it receives to the adjacent more slowly moving layers, there results a steady diminution in the velocity of flow from the most rapidly moving layer A to the layer which is at rest B.

From this model of viscous flow in liquids it is possible to deduce the effects of changes in concentration, pressure, temperature, and size of the molecules. The number of collisions of the particles of one layer with those of another layer, due to translational velocity, will be directly proportional to the rate of shear between the layers. This is the fundamental law of viscous flow. It will also be directly proportional to the number of molecules in each layer, *i.e.* to the concentration. It is a confirmation of this prediction, that we find that the fluidity is decreased in just the proportion that the concentration is increased either by lowering the temperature or by raising the pressure. It is significant that the temperature by itself is without effect on collisional viscosity. The reason for this is evidently that the mere vibration of the molecules without diffusion through successive layers does not affect the rate at which the molecules of one layer overtake the molecules of an adjacent layer moving more slowly. It is

clear that collisional viscosity will increase not only with the concentration but also with the size of the molecules. If the particles were mere points, there would be no collisions and therefore no collisional resistance to flow. On the other hand, if the molecules completely filled the space they occupy, collisions would be most rapid and the collisional resistance a maximum.

The discovery of Batschinski, that in unassociated liquids the fluidity is directly proportional to the free volume, seems to indicate that collisional viscosity is almost entirely responsible for the viscosity of ordinary liquids and it must be highly important in compressed gases. It is also clear why associated liquids are exceptional. For the breaking down of association, as by heating, would doubtless decrease the size of the molecules without a corresponding decrease in the space which they occupy.

The Mixed Régime.—It has been indicated that in rarefied gases viscous resistance is certainly diffusional and in very viscous liquids it is collisional. In fluids at ordinary temperatures and pressures the viscous resistance is evidently the sum of the diffusional and the collisional resistances. The total viscous resistance is in every case given by the equation

$$\eta = \eta_d + \eta_o \tag{57}$$

where η_d is the diffusional viscosity and η_c is the collisional viscosity.

According to Maxwell, as discussed in Chapter XIV, the viscosity of a gas varies as the absolute temperature, so

$$\eta_d = BT$$

where B is a constant. Later experimenters have found that this formula does not accord with the experimental facts, and they have therefore given to the temperature T an exponent n with values varying from the theoretically deduced 0.5 to 1.0. The discrepancy, however, may be due to the fact that collisional viscosity has been overlooked. For diffusional viscosity we here assume as a first approximation that $n = 1$.

We have seen that Batschinski's formula represents collisional viscosity only, which we may now write in the form

$$\eta_o = \frac{A}{v - \omega}.$$

TABLE XXXIX.—THE FLUIDITY OF CARBON DIOXIDE AS CALCULATED BY MEANS OF THE FORMULA $\varphi = (v - \omega)[A + BT\,(v - \omega)]$ WHERE $w = 0.841$, $A = 0.000,257,8$, AND $B = 4{,}998$ COMPARED WITH THE VALUES OBSERVED BY PHILLIPS AT VARIOUS TEMPERATURES AND PRESSURES

Temperature, absolute	Pressure in atmospheres	v	φ observed	φ calculated	Per cent, difference
293	83.0	1.198	1,215	1,152	− 5
	72.0	1.232	1,297	1,241	− 4
	59.0	1.302	1,435	1,418	− 1
	56.0	5.263	5,376	4,890	− 9
	50.0	6.897	5,650	5,299	− 6
	40.0	10.000	6,024	5,734	− 5
	20.0	27.780	6,410	6,421	0
	1.0	546.400	6,757	6,907	+ 2
303	110.5	1.258	1,299	1,300	0
	104.0	1.280	1,364	1,355	− 1
	96.0	1.316	1,443	1,441	0
	90.0	1.346	1,555	1,512	− 3
	82.0	1.397	1,689	1,519	−11
	80.0	1.416	1,770	1,668	− 6
	76.0	1.471	1,890	1,784	− 6
	74.0	1.506	2,020	1,855	− 8
	73.0	1.531	2,092	1,906	− 9
	72.0	1.575	2,183	1,992	− 9
	70.0	3.484	4,367	4,021	− 8
	60.0	5.650	5,348	4,887	− 9
	40.0	10.870	5,952	5,654	− 5
	20.0	28.250	6,289	6,086	− 3
	1.0	565.000	6,536	6,594	+ 1
305	120.0	1.266	1,269	1,318	+ 4
	112.0	1.287	1,350	1,369	+ 1
	104.0	1.316	1,439	1,439	0
	93.0	1.372	1,595	1,568	− 2
	87.0	1.429	1,706	1,693	− 1
	84.0	1.466	1,786	1,771	− 1
	80.0	1.527	1,894	1,894	0
	76.0	1.675	2,232	2,168	− 3
	75.0	1.802	2,463	2,379	− 3
	74.0	2.778	3,937	3,506	− 8
	70.0	3.922	4,673	4,240	− 9
	60.0	5.882	5,348	4,918	− 8
	40.0	11.111	5,714	5,641	− 1
	20.0	28.410	6,173	6,201	0
	1.0	568.100	6,452	6,553	+ 2
308	114.5	1.324	1,443	1,455	+ 1
	109.0	1.349	1,515	1,512	0
	96.0	1.437	1,706	1,706	0
	88.0	1.531	1,957	1,896	− 3
	85.0	1.597	2,193	2,021	− 8
	80.0	2.024	2,770	2,690	− 3
	75.0	3.460	4,219	3,966	− 6
	70.0	4.405	4,673	4,425	− 5
	60.0	6.135	5,618	4,943	−12
	40.0	11.765	5,747	5,642	− 2
	20.0	28.740	6,135	6,135	0
	1.0	574.700	6,410	6,487	+ 1
313	112.0	1.431	1,751	1,686	− 4
	108.0	1.466	1,852	1,759	− 5
	100.0	1.572	2,070	1,965	− 5
	94.0	1.718	2,415	2,221	− 8
	85.0	2.597	3,717	3,302	−13
	80.0	3.436	4,587	3,920	−14
	70.0	4.902	5,000	4,553	− 9
	60.0	6.536	5,348	4,964	− 7
	40.0	12.050	5,682	5,585	− 2
	23.8	24.510	5,917	5,987	+ 1
	1.0	578.000	6,369	6,385	0

where A and ω are constants and v is the specific volume in ml per gram. We have then

$$\eta = BT + \frac{A}{v - \omega}$$

or

$$\varphi = \frac{v - \omega}{A + BT(v - \omega)}. \tag{58}$$

It is truly remarkable that so simple an equation as this can be employed with success to reproduce so complex data as that for the fluidity isothermals of carbon dioxide passing through the critical state. To what extent it does do this is shown in Table XXXIX. Since the calculated values are nearly all too small, it is evident that a better concordance could have been secured by a happier choice of constants, but considering the difficulties in these measurements, the percentage of deviation between the calculated and the observed values is not large.

Having established a fairly exact relationship between fluidity and volume, and indirectly with temperature and pressure, the problem of associated substances again presses itself into the foreground as it tends to do so often. A means must be found for bringing these substances into conformity with the others, but the solution is not yet forthcoming.

Dr. Kendall inquires in regard to the foregoing:— "Is the formula of Batschinski of such great importance as your extended treatment of it would lead the readers to believe? Is it not merely an interpolation formula? Would it not be well to mention something about the alternative formula of Arrhenius?" (1918). The expotential formula of Arrhenius (1918) does not lead us to a definite mental picture, and like many another frankly empirical formula was omitted in this brief treatment of the subject. The relation of Batschinski fills a need which was felt in many minds, *cf.* p. 142. It leads us at once to a definite mental picture which is neccessary in building up a consistent theory, so that we are now able to explain the relation of fluidity to volume, temperature and pressure *et cet.* in a manner which is so natural, so unexpectedly simple and so beautifully in accord with observed facts that it is hard to see what more evidence is needed to carry conviction.

CHAPTER IV

FLUIDITY AND VAPOR PRESSURE

All physical and chemical properties will perhaps in time be shown to be related so that the knowledge of a certain set of facts in regard to a substance, such for example as its chemical structure, will enable one to deduce it multitudinous properties. Thus having established a direct causal dependence of the fluidity upon the volume, it is also important to study other properties which depend upon the fluidity, or which together with the fluidity depend upon a common cause. Migration velocity and electrical conductivity of solutions are examples of properties which are directly dependent upon the fluidity. There are properties which are not dependent upon the fluidity directly but which with the fluidity are dependent upon the same property and therefore are indirectly related. The boiling-point, the critical temperature and the vapor-pressure are properties of this latter type, which we will now consider.

Fluidity and Boiling-point.—On examination of the fluidity-temperature curves of the aliphatic hydrocarbons, Fig. 41, and ethers, Fig. 42, we note that the fluidities of these substances at their boiling-temperatures—shown by small circles—are nearly identical. It is perhaps of no special significance that the fluidities are identical, but it *is* important that the line connecting the fluidities at the boiling-points is linear. This linear character of the fluidity-boiling-point curve is exemplified by the aliphatic chlorides, bromides and iodides as well as by the ethers and hydrocarbons. The acids and alcohols are again exceptional.

The meaning of this relation may be most easily grasped by reference to Fig. 42. If we assume that the curves of the members of a given class have the same slope and the same degree of curvature at the boiling-point, it is evident that the addition of a methylene group to a molecule causes a rise in the boiling-point Γ measured by AC^1 or CE, but at the same time

[1] *Cf.* Fig. 42.

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the addition of a methylene group causes a decrease in the fluidity Δ which is AB or CD. It appears that $AC/AB = CE/CD$, so the ratio between the effect produced on the boiling-point to the effect produced on the fluidity Γ/Δ is constant, for this particular homologous series. This relation does not apply to the alcohols and acids. A reason is that as the temperature is raised, the association is lowered, Γ becomes smaller and at the same time Δ becomes greater, so that their ratio may vary.

Fluidity and Vapor Pressure.—If there is a relation between the fluidity and the boiling-point, it is evident that a more
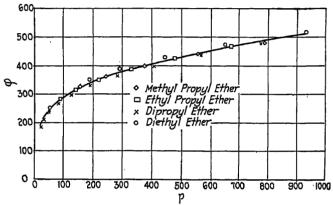
FIG. 58.—Fluidity-vapor pressure curves of a series of ethers.

general relation than the above can be obtained by comparison at other vapor pressures than at the ordinary boiling temperature. Thus if all of the aliphatic ethers have the same fluidity at the ordinary boiling-point, and the same were true at other vapor pressures, it follows that, when the vapor pressures corresponding to a given temperature are plotted against the fluidities corresponding to that temperature, and this process is repeated for a series of temperatures, the curves of all of the substances of the class should fall together; in other words, the fluidity vapor-pressure curve of one ether ought to be the curve of all the other members of the class. Conversely, if either the vapor pressure or the fluidity of an ether is known for a given temperature, the other quantity, supposedly unknown, can be determined by means of

the fluidity vapor-pressure curve of the class. Not only do all the members of this class fall together in a single parabolic curve, shown in Fig. 58, but substances of other classes give a curve of similar form, as will now be demonstrated.

If we take a single substance, such as heptane, as our standard

TABLE XL.—FLUIDITIES AND VAPOR PRESSURES CORRESPONDING TO THE
STANDARD FLUIDITY VAPOR-PRESSURE CURVE

Fluidity reduced	Vapor pressure in mm	Fluidity reduced	Vapor pressure in mm	Fluidity reduced	Vapor pressure in mm
100	0.5	310	111.1	420	396.7
110	0.7	315	119.0	425	415.7
120	1.0	320	127.8	430	434.9
130	1.7	325	136.5	435	455.5
140	2.2	330	146.1	440	476.1
150	3.0	335	155.4	445	497.3
160	4.3	340	165.2	450	520.0
170	6.1	345	175.5	455	542.2
180	8.2	350	186.2	460	566.8
190	11.0	355	197.6	465	589.5
200	14.2	360	210.4	470	614.7
210	17.7	365	223.2	475	635.9
220	22.3	370	236.6	480	660.1
230	27.7	375	251.0	485	683.7
240	34.1	380	266.0	490	711.7
250	41.2	385	281.1	495	736.3
260	49.3	390	296.2	500	760.0
270	58.8	395	311.4	505	783.8
280	69.1	400	328.3	510	810.0
290	81.8	405	344.7	515	838.8
300	95.9	410	360.7	520	869.5
305	103.2	415	378.4	525	902.0

substance with a fluidity of approximately 500 at the boiling-point, we can compare other substances with this one. Since other substances do not have the same fluidity at the boiling-point, we multiply the fluidity at the boiling-point by a factor so that the product or the reduced fluidity will be 500. The fluidities for other temperatures are also reduced by similarly

multiplying by the *same* factor.   Since the fluidity vapor-pressure curves pass through the origin and we by this process bring them
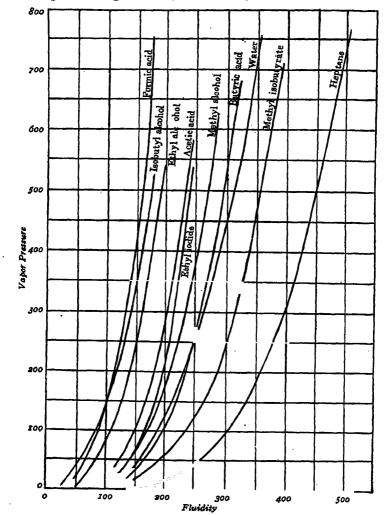
FIG. 59.—The vapor-pressure curves of some associated substances compared with heptane.

together at the boiling-point, a comparison of the reduced values for other temperatures with the values for heptane will show how nearly similar are the curves for different substances, even

when they belong to very different classes. For 17 substances compared by this method, the average deviation between the observed and calculated values is approximately 3 per cent, so long as the vapor pressure is above 10 cm.

A few examples will serve to make the use of the method clear. Thus the fluidity of ethyl acetate at its boiling-point (77.2°C) is 395.6 and the reduction factor is therefore $500/395.6 = 1.264$. The fluidity of the substance as determined by Thorpe and Rodger for 30° is 249.9 and the reduced fluidity is therefore $249.9 \times 1.264 = 315.8$, and the vapor pressure read from the Table XL for the standard curve corresponding to this fluidity is 120.4 mm, while the vapor pressure observed by Young is 118.7 mm. As a further example, ethyl propyl ether has a fluidity of 479.9 at its boiling-point (63.4°). The factor is $500/479.9 = 1.042$. The fluidity at 20° as determined by Thorpe and Rodger is 314.9 and this reduced is $314.9 \times 1.042 = 328.1$, and according to the Table XL this corresponds to 142.5 mm which is practically identical with the experimental value of 142.6.

Associated substances do not show the relation between fluidity and vapor pressure shown elsewhere. The greatest deviation is shown by isobutyl alcohol and formic acid and ethyl alcohol. In Fig. 59, there is plotted the vapor-pressure-temperature curve of heptane (not reduced) with several "associated" substances which show large deviation from the standard. We note that isobutyl alcohol, formic acid, and ethyl alcohol show the most rapid increase in the vapor pressure. This is added evidence of the breaking down of association. (*Cf.* pp. 276 and 277.)

Before concluding our consideration of vapor pressure it may be remarked that since fluidity is related to volume and at the same time to vapor pressure, there is necessarily a relation between volume and vapor pressure. The volume is doubtless affected by the internal forces between the molecules which we ordinarily call cohesion and vapor pressure naturally depends upon the same. So there may quite possibly be a connection between fluidity and cohesion, even though it is not the connection which is often supposed.[1]

Cf. p. 147 *et seq.*

CHAPTER V

THE FLUIDITY OF SOLUTIONS

The fluidity curves of solutions are most logically considered under four types: I. In the simplest case the fluidity of the mixture can be calculated from the fluidities of the components. There is no volume change on mixing, and it is assumed that the components neither dissociate nor interact with each other on mixing. The method of calculation of the fluidity of the ideal mixture has been the subject of much discussion and it will be discussed presently. Examples of this simplest type are carbon tetrachloride and benzene, and diethyl ether and benzene.

Thorpe and Rodger (1897) found that there was a very slight contraction on mixing carbon tetrachloride and benzene, thus confirming the earlier observation of F. D. Brown. In the case of methyl iodide and carbon disulfide there was a very slight expansion which decreased as the temperature was raised. Ramsay and Aston found that the surface tension of mixtures of carbon tetrachloride and benzene followed the mixture rule. Zawidski furthermore observed that the vapor pressures of these same mixtures showed but a slight deviation from the mixture rule, due, according to Dolazalek, to association of the carbon tetrachloride. This is the sort of parallelism which needs much further investigation because it affords the most nearly indisputable evidence to aid the investigator in the selection of ideal mixtures. In much of our physico-chemical reasoning, it would beyond any question be a great advantage if we could assume certain mixtures as ideal in the sense defined above.

The fluidity-volume concentration curves of this class are nearly but not quite linear, as will be explained.

II. There are instances where there is a well-defined expansion on mixing, accompanied with heat absorption, and in such mixtures we generally find the fluidity greater than calculated. The fluidity-volume concentration is convex upward, i.e., the curvature $d^2\varphi/dc^2$ is negative. The increase in fluidity may be

attributed to breaking down of association or to dissociation which also give rise to the increase in volume. Benzene and ethyl acetate may be cited as an example of this type.

III. When two liquids are mixed, perhaps more often than not, there is a decrease in the volume, particularly in aqueous solutions. With this decrease in volume there goes a positive heat effect and a decrease in the fluidity, so the fluidity-volume concentration curves are convex downward, *i.e.*, $d^2\varphi/dc^2$ is positive. Since the fluidity changes some 2,000 times as rapidly as the free volume, as shown by Batschinski's law, the effects of the solvation which is presumed to be present in this case manifest themselves far more prominently in the fluidity data than in the data on volume. Examples of this type are very common, making up the greater portion of aqueous mixtures, such as ethyl alcohol and water, acetic acid and water and many mixtures of organic liquids such as chloroform and ether. In some cases there is incontestible proof that a chemical compound is formed on mixing, as when aniline is mixed with acetic acid. In other cases, the formation of hydrates or solvates is very probable. Whether there is a sharp line to be drawn between the forces of cohesion of a purely physical nature and the forces which bring about actual chemical combination must be decided by future experiment.

IV. When associated solvents break down, to later unite with each other, we have a combination of the second and third types. The resulting curve may then show positive curvature over part of its course and negative curvature over a part, there being a point of inflection. Examples of this type are found in both aqueous and non-aqueous solutions, ammonium nitrate solutions being a good example of the former.

Instances of this type are instructive, since they put us on our guard against assuming that because a given mixture displays strong positive curvature, dissociation is not a factor. A pair of liquids may fall into type II and yet have a tendency to unite together chemically, provided merely that the effect of dissociation predominates in all mixtures.

Again the opposing effects may be nearly equal at all concentrations, as is true of ethyl alcohol and acetone, and formic acid and water. These mixtures evidently fall under type IV and not

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type I, but in cases of doubt resort may be had to a study of the other physical properties.

I. The Ideal Mixture

If there is no contraction on mixing two liquids
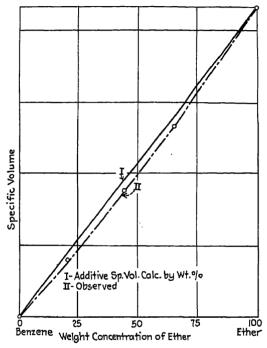
Fig. 60.—Specific volume-weight concentration curve of mixtures of benzene and ether. (*After D. F. Brown.*)

$$v = mv_1 + nv_2 = \frac{1}{\rho} = \frac{1}{a\rho_1 + b\rho_2} \tag{59}$$

where v is the specific volume and ρ the density of the mixture, containing m weight fraction or a volume fraction of the component A whose specific volume is $v_1 = \frac{1}{\rho_1}$ and n weight fraction or b volume fraction of the component B whose specific volume is $v_2 = \frac{1}{\rho_2}$ So $a = \frac{mv_1}{mv_1 + nv_2}$. From the above equa-

tion it follows that if we plot volumes against weight concentra-
tion, we will obtain a linear curve such as curve I in Fig. 60;
but if we plot specific volumes against volume concentrations,
we will obtain not the linear curve III, Fig. 61, but curve IV.

We have seen that the fluidity of a liquid is directly propor-
tional to its free volume, but the fluidities are additive (Eq. (25))
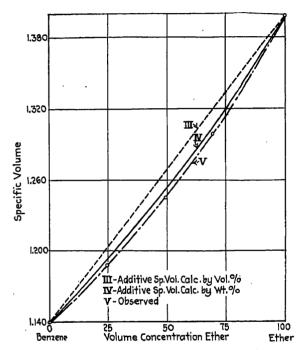
Fig. 61.—Specific volume–volume concentration curve of mixtures of benzene
and ether. (*After D. F. Brown.*)

only when we use volume percentages; hence it follows that if a
pair of liquids on mixing gave a linear specific volume–volume
concentration curve (curve III) they would also give a linear
fluidity–volume concentration curve, curve VI, Fig. 62. Since,
however, the ideal mixture gives a volume–volume concentration
curve which shows positive curvature, the fluidity–volume con-
centration curve of the ideal mixture will also show positive
curvature, curve VII, Fig. 62.

Since this sag in the fluidity curve is due to the mathematical necessities of the case and not to chemical combination or dissociation, it is evidently possible to calculate the fluidity of the mixture from the fluidities and volumes of the components.
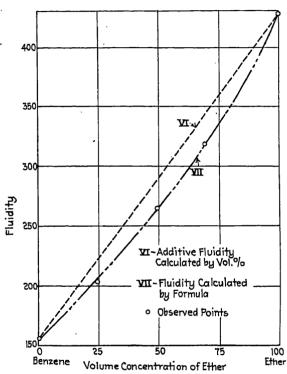
Fig. 62.—Fluidity-volume concentration curve of mixtures of benzene and ether. (*After D. F. Brown.*)

We have seen that the observed specific volume of the mixture is

$$mv_1 + nv_2$$

whereas the specific volume should be

$$av_1 + bv_2$$

in order to give a linear fluidity-volume concentration curve (Eq. (25)), so the specific volume is too small by an amount represented by the *specific volume difference*, Δv.

$$\Delta v = av_1 + bv_2 - mv_1 - nv_2$$
$$= (a - m)v_1 - (n - b)v_2$$
$$= (a - m)(v_1 - v_2) \tag{60}$$

since $\qquad a - m = n - b.$

If the fluidity is directly proportional to the free volume (Eq. 56), it seems reasonable to assume that if the volume is decreased for any reason by an amount Δv, the fluidity will be decreased by an amount which is some function of this $f\Delta v$. Since in the ideal mixture the fluidity is only slightly less than that given by the linear formula (Eq. 25), we may assume as a first approximation that the decrease in fluidity is directly proportional to the specific volume difference. We then obtain as our formula for the true fluidity Φ

$$\Phi = k(v - w) - K\Delta v$$
$$= \varphi - K\Delta v$$
$$= a\varphi_1 + b\varphi_2 - K(a - m)(v_1 - v_2). \tag{61}$$

It may be possible later to evaluate the above function, but it is only necessary to know the fluidity of one or more mixtures in order to determine a value for the constant K, from which the fluidities of all other mixtures of the two components may be calculated. The physical significance of K will be explained later.

We may take for an example carbon tetrachloride and benzene, the mixtures of which were studied carefully by Thorpe and Rodger, and at a single temperature by Linebarger. (*Cf.* Table XLII.) In the first line at each temperature are given the fluidities observed. In the second line are given the fluidities (Φ) as calculated with the use of Eq. (61), using 40 as the value for K. The fluidities (φ) as given by the simple additive formula, Eq. (25), are given in the third line. These last are invariably higher than the observed values, but when corrected for the volume the agreement is very close, the average deviation being less than half of 1 per cent.

It is worth noting in passing to what extent Batschinski's Law applies to the ideal mixture, with which we assume to be dealing in this case. Using the limiting specific volumes of carbon tetrachloride and benzene as 0.5782 and 1.0476 respectively, we have calculated the values of ω by the admixture rule to be 0.683, 0.784, and 0.896, using weight percentages. This accords

perfectly with the values 0.683, 0.785, and 0.897 obtained from the observed fluidity data for each mixture. The values of k in the Batschinski formula are 2,019, 1,937, 1,845 as calculated from the pure solvents, as compared with 2,034, 1,993, and 1,876 as obtained from the data for the mixtures. The values of the fluidities calculated by means of the former set of constants are not so close to the observed values as are the values calculated by the corrected fluidity formula. But they are at least as close to the observed values of the mixtures as the calculated fluidities of pure carbon tetrachloride are to the observed.

It is impracticable here to consider in detail all of the examples

TABLE XLI.—SPECIFIC VOLUMES IN MILLILITERS PER GRAM OF MIXTURES OF CARBON TETRACHLORIDE AND BENZENE, FROM THORPE AND RODGER

Temperature	Per cent benzene by weight					
	0	22.37	43.79	67.71	100	
	Per cent benzene by volume					
	0	34.30	58.54	79.17	100	
0	0.6127	0.7238	0.8304	0.9497	1.1109	Observed
	......	0.7242	0.8309	0.9501	......	Calculated
10	0.6202	0.7326	0.8405	0.9610	1.1242	Observed
	......	0.7329	0.8412	0.9614	......	Calculated
20	0.6278	0.7415	0.8508	0.9728	1.1377	Observed
	......	0.7418	0.8511	0.9730	......	Calculated
30	0.6355	0.7508	0.8613	0.9846	1.1514	Observed
	......	0.7509	0.8615	0.9849	......	Calculated
40	0.6435	0.7602	0.8724	0.9971	1.1661	Observed
	......	0.7604	0.8723	0.9973	......	Calculated
50	0.6518	0.7700	0.8836	1.0099	1.1812	Observed
	......	0.7702	0.8836	1.0103	......	Calculated
60	0.6604	0.7801	0.8951	1.0231	1.1966	Observed
	......	0.7803	0.8952	1.0234	......	Calculated
70	0.6694	0.7907	0.9071	1.0369	1.2124	Observed
	......	0.7909	0.9072	1.0371	......	Calculated

TABLE XLII.—THE FLUIDITIES OF MIXTURES OF CARBON TETRACHLORIDE AND BENZENE FROM THORPE AND RODGER[1] AND FROM LINEBARGER[2]

Temperature	Per cent benzene by weight (100n)					
	0	22.37	43.79	67.71	100	
	Per cent benzene by volume (100b)					
	0	34.30	58.54	79.17	100	
0	74.1	83.6	91.9	100.6	110.8	Fluidity observed
	.....	84.3	92.7	100.9	.....	ϕ calculated, Eq. (61)
	.....	86.7	95.6	103.2	.....	φ calculated, Eq. (25)
	72.6	82.2	90.4	99.1	108.9	Fluidity calculated Eq. (54)
10	88.2	100.0	110.1	120.2	131.5	Observed
	.....	100.6	110.6	120.2	.....	ϕ calculated, Eq. (61)
	.....	103.0	113.5	122.5	.....	φ calculated, Eq. (25)
	88.4	99.9	110.0	119.9	131.8	Calculated Eq. (56)
20	103.2	117.6	128.9	141.4	154.1	Observed
	.....	118.3	130.0	141.2	.....	ϕ calculated, Eq. (61)
	.....	120.7	133.0	143.5	.....	φ calculated, Eq. (25)
	104.4	117.9	130.0	141.7	155.1	Calculated Eq. (56)
30	118.9	136.2	149.0	163.4	178.0	Observed
	.....	136.8	150.5	163.4	.....	ϕ calculated, Eq. (61)
	.....	139.2	153.5	165.7	.....	φ calculated Eq. (25)
	120.6	136.7	150.3	163.5	178.6	Calculated Eq. (56)
40	135.5	156.0	171.5	186.6	203.1	Observed
	.....	156.2	172.0	186.6	.....	ϕ calculated, Eq. (61)
	.....	158.7	175.1	189.0	.....	φ calculated, Eq. (25)
	137.5	155.7	171.8	186.3	203.9	Calculated Eq. (56)
50	153.0	176.7	194.9	211.4	228.8	Observed
	.....	176.5	194.2	210.6	.....	ϕ calculated, Eq. (61)
	.....	179.0	197.4	213.0	.....	φ calculated, Eq. (25)
	154.9	175.5	193.5	210.3	229.9	Calculated Eq. (56)
60	171.5	198.8	219.3	237.0	256.1	Observed
	.....	198.0	217.8	236.1	.....	ϕ calculated, Eq. (61)
	.....	200.5	221.0	238.5	.....	φ calculated, Eq. (25)
	173.0	195.9	215.8	234.3	256.4	Calculated Eq. (56)
70	191.0	.....	243.3	263.9	284.9	Observed
	.....	.....	242.8	262.9	.....	ϕ calculated, Eq. (61)
	.....	.....	246.0	265.4	.....	φ calculated, Eq. (25)
	192.0	.....	239.0	260.1	288.6	Calculated Eq. (56)
Value of k........	2,105[3]	2,019	1,937	1,845	1,721[3]	
Value of ω........	0.5782[3]	0.6831	0.7837	0.8960	1.0476.	

Temperature	Per cent benzene by weight					
	0	13.73	40.78	58.60	100	
25	113.2	123.8	141.6	151.5	166.9	Linebarger observed
	111.0	121.8	137.2	147.1	166.7	Thorpe and Rodger observed

[1] *J. Chem. Soc.* (London), **71**, 364 (1897).
[2] *Am. J. Sci.* (4), **11**, 331 (1896).
[3] Batschinski, *Zeitschr. f. physik. Chem.*, **84**, 643 (1913). Calculated on the basis of Young's specific gravities.

which have been studied lately. Kendall and Wright and many others have done valuable service; they have chosen inert liquids whose individual fluidities are widely separated, hence these mixtures are suited to give a crucial test of the mixture formulas.

Delbert F. Brown has studied this data to determine (1) whether the volume difference Δv is greatest when the specific gravities of the components are most widely different, (2) whether the fluidity difference $\Delta \varphi$ is greatest in the same mixtures in which the volume difference is greatest, (3) whether those pairs of liquids showing the greatest volume difference also show the greatest fluidity divergence, and (4) whether the fluidities of the mixtures can be calculated from the fluidities and volumes of the components. Table XLIII gives a summary of part of his results. The table is so arranged that the differences between the specific volumes of the components, column 2, are in the order of increas-

TABLE XLIII.—FLUIDITY AND VOLUME RELATIONS IN CERTAIN IDEAL MIXTURES (USING DATA OF KENDALL AND WRIGHT)

Components	Specific volume difference of components $v_2 - v_1$	Specific volume difference Δ_v	Fluidity difference $\Delta \varphi$	Average deviation in per cent
Ethyl benzoate and benzyl benzoate....................	0.0594	0.0010	5.04	1.0
Phenetol and diphenyl ether....	0.1056	0.0028	5.58	0.56
Ethyl acetate and ethyl benzoate	0.1616	0.0062	25.9	1.2
Ethyl acetate and benzyl benzoate	0.2183	0.0118	55.05	9.2
Diethyl ether and phenetol......	0.3610	0.0268	60.3	1.2
Diethyl ether and diphenyl ether	0.4666	0.0458	110.5	3.8

ing magnitude. The third column shows that the sag in the volume-volume concentration curve follows exactly this order of increase, and column 4 shows that the fluidity divergence $\Delta \varphi$ follows the same order of increase. Moreover, the maximum divergence in both the volumes and the fluidities occurs in the same mixture in every case, except that of diethyl ether and diphenyl ether, although it is not possible to bring this out in the table. The last column shows the average deviation of the values of the fluidity, as calculated by Brown from the data of Kendall and Wright by the formula (61). In only two cases is

this deviation much over 1 per cent. Brown found that the deviation is usually larger in mixtures which contain an ester as one or both of the components. This, however, is not shown by this table very well, but if the conclusion is correct, the deviation would be explained by the chemical character of the components. This brings us to the consideration of the non-ideal types of mixtures.

The reader will perhaps ask whether the fluidities of ideal mixtures would be additive if plotted against weight concentrations. The curves for carbon tetrachloride and benzene have been published,[1] using both volume and weight concentrations. Using volume concentrations the curves are slightly sagged as already pointed out, but using weight concentrations they show marked *negative* curvature particularly at the higher temperatures. The very slight contraction of carbon tetrachloride and benzene on mixing in no way accounts for this negative curvature.

II. Negative Curvature and Dissociation by Dilution

We will now consider a pair of substances which expand on mixing, using the data of Thorpe and Rodger for methyl iodide and carbon disulphide. The curvature of the fluidity-volume concentration curves is negative and greatest at the lowest temperatures. This is in accordance with the view that the components are less associated at the higher temperatures and therefore can show less dissociation on mixing.

The expansion on mixing amounts to as much as 0.2 per cent of the volume, as may be seen by comparing the observed specific volumes with those calculated by the admixture rule, Table XLV. The fluidities are given in Table XLIV and it is seen that Batschinski's Law applies to each mixture, but the values of the limiting specific volumes ω cannot be calculated by the admixture rule as in the normal mixture. The actual limiting volume is some 2 per cent less than the calculated value, presumably due to the dissociation. The values of k, which measure the slope $\dfrac{\varphi}{v - \omega}$ of the fluidity-specific volume curves are very much less

[1] *Zeitschr. f. physik. Chem.*, **83**, 657 (1913).

than the calculated values.   This is also in marked contrast to
the case of carbon tetrachloride and benzene.

TABLE XLIV.—THE FLUIDITIES OF MIXTURES OF METHYL IODIDE AND
CARBON DISULPHIDE (FROM THORPE AND RODGER)

Temperature	Per cent carbon disulphide by weight							
	0	21.60	38.81	48.11	68.81	82.39	100	
	Per cent carbon disulphide by volume							
	0	32.22	53.39	62.61	79.94	89.42	100	
0	168.3	193.1	207.5	213.2	222.7	228.3	232.8	Observed
	168.6	193.0	207.5	212.5	223.1	228.7	233.1	Calculated, Batschinski
	.....	192.3	207.6	213.3	223.0	228.4	.....	Calculated, Gibson
10	186.6	211.4	225.7	225.9	242.1	248.1	253.0	Observed
	186.2	211.3	225.6	230.5	241.6	248.0	252.1	Calculated, Batschinski
	.....	211.1	225.7	230.0	242.0	248.0	.....	Calculated, Gibson
20	205.3	230.9	243.9	248.1	261.8	268.1	272.5	Observed
	205.3	230.4	243.8	248.5	260.6	268.0	271.9	Calculated, Batschinski
	.....	229.2	244.0	248.2	262.0	268.0	.....	Calculated, Gibson
30	224.8	250.6	263.2	267.4	280.1	288.2	293.5	Observed
	224.7	250.2	262.8	267.0	280.0	288.2	292.2	Calculated, Batschinski
	.....	250.8	263.2	268.0	281.0	288.0	.....	Calculated, Gibson
40	244.7	271.0	282.5	285.7	299.4	309.6	314.0	Observed
	244.8	270.2	282.3	286.2	300.1	309.8	318.4	Calculated, Batschinski
	.....	270.8	282.6	286.0	300.0	309.5	.....	Calculated, Gibson
Value of ω from mixtures....	0.3808[1]	0.4405	0.4855	0.5096	0.5722	0.6161	0.6642	
from solvents....	......	0.4420	0.4908	0.5171	0.5758	0.6143	......	
Value of k from mixtures....	3,527[1]	3,040	2,633	2,465	2,341	2,322	2,123	
from solvents....	......	3,224	2,982	2,852	2,561	2,370	.....	

[1] Using the densities of Thorpe and Rodger we have recalculated these constants, instead of taking the values of Batschinski.

When there was a volume change on mixing, Gibson assumed
that the specific volumes v_1 and v_2 were not the same as for the

components. He assumed that the free volume per unit of limiting volume was the same for each kind of molecule, so that from the equations

$$\frac{v_1}{\omega_1} = \frac{v_2}{\omega_2} = \ . \ . \ .$$

and

$$v = mv_1 + nv_2$$

the values of v_1 and v_2 could be calculated. He then calculated the fluidities of the mixture by means of the simple additive fluidity formula (25). That the values calculated by Gibson agree well with the observed is shown in the third line of fluidities for each temperature given in Table XLIV.

TABLE XLV.—THE SPECIFIC VOLUMES IN MILLILITERS PER GRAM OF MIXTURES OF METHYL IODIDE AND CARBON DISULPHIDE (FROM THORPE AND RODGER)

Temper-ature	Per cent carbon disulphide by volume							
	0	33.22	53.39	62.61	79.94	89.42	100	
0	0.4285	0.5040	0.5643	0.5959	0.6675	0.7146	0.7740	Observed
	......	0.5031	0.5624	0.5945	0.6659	0.7128	......	Calculated
10	0.4336	0.5100	0.5712	0.6031	0.6754	0.7229	0.7830	Observed
20	0.4390	0.5163	0.5781	0.6104	0.6835	0.7315	0.7923	Observed
	......	0.5152	0.5759	0.6087	0.6817	0.7297	......	Calculated
30	0.4445	0.5228	0.5853	0.6179	0.6918	0.7412	0.8018	Observed
40	0.4502	0.5295	0.5927	0.6257	0.7004	0.7495	0.8118	Observed
	......	0.5282	0.5904	0.6242	0.6987	0.7475	......	Calculated

We have come now to the case where there is chemical combination on mixing. There is generally a decrease in volume and the specific volume-weight concentration curve, curve II, Fig. 60, is sagged as well as curve V, Fig. 61, representing the specific volume-volume concentration curve. Since new substances are formed, no method given thus far can be depended upon for calculating the fluidity-volume concentration curve.

III. Positive Curvation and Chemical Combination

Before considering the meaning of positive curvature in detail, it is necessary to emphasize the fact that a *minimum* in the fluidity-volume concentration curve is not necessary to indicate that chemical combination is taking place and when a minimum does occur, its location, according to numerous investigators, notably Findlay (1909) and Denison (1913), does not correspond to the exact composition of the compound formed. This is proved, if proof be needed, by the fact that the minimum usually changes with the temperature and may disappear altogether. The question then is, assuming that a chemical combination is formed by the mixing of the two components of a binary mixture, how can the data be used to show what this compound is? To answer this, we will present three cases of increasing complexity, in all of which there is the same amount of chemical combination, it being assumed that in the feeble combination with which we are dealing the two components A and B are always in equilibrium with a small amount of the compound C so that

$$A + B \rightleftarrows C$$

Case I.—The fluidity-temperature curves of two closely related substances are represented by the curves A and B in Fig. 63a. If there were no combination between the components on mixing, the curve for the 50 per cent mixture would lie half-way between the curves A and B (dotted). Let it be assumed that this mixture does show the maximum amount of combination and that the curve is thereby lowered to $0.5B$. Using the data plotted in Fig. 63a it becomes possible to plot the fluidity-volume concentration curves for the various temperatures t_1, t_2, t_3, etc., as shown in Fig. 63b. In this case there is a well-defined minimum in the fluidity-volume concentration curve in the 50 per cent mixture and the deviation of the curves from the normal (dotted) curves is constant in amount.

Case II.—Let us now assume that we are dealing with two substances whose fluidities are widely different, although they still run parallel to each other. With the same amount of combination as before, the curve $0.5B$ falls between the curves A and B, Fig. 64a. As a result the fluidity-volume concentration curves, Fig. 64b, no longer exhibit a minimum although, by assumption,

the hydration is the same as before both in relative composition and amount. However, it is clear that the deviation of the fluidity
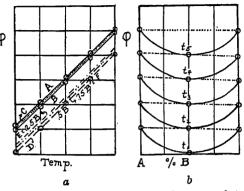
FIG. 63.—Diagram to illustrate the fact that when two substances A and B of similar fluidity are mixed, the formation of a solvate produces a minimum in the fluidity-concentration curves.
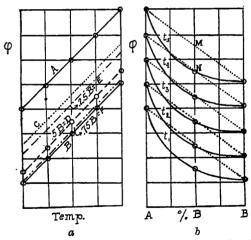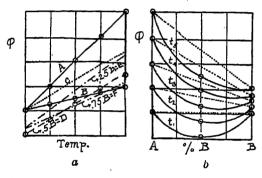
FIG. 64.—Diagram illustrating how when two substances A and B are mixed whose fluidities are very different, the formation of a solvate produces no minimum in the fluidity-concentration curve.

volume concentration curves from the linear curves, which would be expected were there no combination, and as indicated in the figures by the distance MN, is the same as in the preceding case.

Case III.—In the usual case in practice, the fluidity-temperature curves are not parallel, so that the fluidities may be identical at one temperature but very different at another. We then obtain a series of curves as shown in Fig. 65a and 65b. At low temperatures there is a good minimum in the fluidity-volume concentration curves, but it gradually shifts to the right as the temperature is raised, until at the highest temperatures it disappears altogether. It is manifestly erroneous to assume that the composition of the hydrate changes on this account. On the other hand, the deviation from the expected linear curves as

FIG. 65.—Diagram illustrating how the minimum in the fluidity-concentration curve may shift with the temperature. The maximum deviation from the linear curve is the significant quantity. This quantity does not vary with the temperature and it indicates the composition of the solvate.

measured vertically is everywhere the same as in the simpler cases. In practice, the hydration is generally less at the higher temperatures so that the deviation should grow less as the temperature is raised, but the cases already given are sufficient to show that the *deviation* of the observed fluidity-volume concentration curve from the linear curve, which would be expected were there no combination between the components of the solution, can alone furnish trustworthy information.

Were the components of the mixture non-associated, it seems possible to calculate not only the composition of the solvate formed but also the percentage of it existing in the solution. But substances which form feeble combinations on mixing are usually themselves associated, and it is quite likely that this

association is altered in the mixture, so that the result is considerably complicated thereby. We have, however, a fairly simple case in mixtures of ether and chloroform studied by Thorpe and Rodger. Chloroform, like carbon tetrachloride, is probably slightly associated but ether may be regarded as unassociated.

So far as can be learned from their measurements the maximum contraction on mixing occurs in a mixture containing less than 40 per cent of ether and perhaps less than 39 per cent; the maximum deviation of the fluidity-volume concentration curve from the linear curve occurs in the 58 volume per cent mixture ± 3 per cent. This corresponds to 39.8 per cent by weight. A mixture corresponding to the formula $C_4H_{10}O.CHCl_3$ contains 38.30 per cent ether by weight. Guthrie has noted that heat is evolved on mixing and that it is a maximum when the components are in molecular proportions. The vapor-pressure, refractive index and the freezing-point curves all give evidence of the formation of a compound $C_4H_{10}O.CHCl_3$.

In the mixture containing 56.26 volume per cent of ether, or one molecule of ether to one of chloroform, we will now calculate the percentage combined. From the atomic constants already given, p. 126, it appears that the compounds $C_4H_{10}O.CHCl_3$ should have a fluidity of 200 at the absolute temperature of 538.6°. But actually a mixture of this composition has a fluidity of 200 at 282.9° absolute (9.9°C). Pure ether and pure chloroform have fluidities of 200 at 216.5° and 305.3° absolute respectively, so that if the mixture were wholly uncombined, the absolute temperature necessary for a fluidity of 200 would be 216.5 × 0.5626 + 305.6 × 0.4374 = 255.4°. Letting x represent the fraction of the volume of the mixture which is combined, we obtain the equation

$$538.6x + 255.4(1 - x) = 282.9$$

and $x = 0.0971$. Since at this temperature (9.9°C) less than 10 per cent of the volume of the mixture is actually in combination, it seems reasonable to assume that a dynamic equilibrium exists between the combined and the uncombined portions. If the Mass Law holds, we have

$$\frac{[C_4H_{10}O]\ [CHCl_3]}{[C_4H_{10}O\ .\ CHCl_3]} = K$$

where the concentrations are molecular and not volume concentrations.

In the above equimolecular mixture, if we let y represent the number of milliliters of ether which are combined in every 100 ml of mixture, the volume of the chloroform combined will be

$$\frac{0.7366 \times 119.36y}{74.08 \times 1.526} = 0.7777y$$

where the specific gravities of ether ρ_e and chloroform ρ_o are taken as 0.7366 and 1.526 respectively and their molecular weights, m_e and m_o, 74.08 and 119.36. Since the sum of the two volumes $y + 0.7777y$ is 9.71, the volume of the ether combined is 5.46 ml and the volume of the chloroform is 4.25 ml.

Substituting the molecular concentrations in the above formula

$$K = \frac{[(56.26 - 5.46)\rho_e/m_e][(43.74 - 4.25)\rho_c/m_c]}{9.71\rho/(m_e + m_c)} = 4.696$$

where ρ is the density of the compound calculated by averages to be 1.082.

With this value of K, it is possible to calculate the absolute temperature corresponding to a fluidity of 200 for any mixture on the assumption that only one compound is formed and that the Law of Mass Action is obeyed. Thus for any mixture if a is the volume percentage of ether and z is the fraction of the ether which is combined,

$$\frac{\frac{a\rho_e}{m_e} \cdot (1 - z)\left[\frac{(1 - a)\rho_c}{m_c} - \frac{a\rho_e}{m_e}z\right]}{\frac{a\rho_e}{m_e} \cdot z} = 4.696$$

For the 28.21 volume per cent ether mixture, $z = 0.157$. The volume of ether in 100 ml which is combined is $az = 4.43$ ml, and the volume of chloroform combined is $0.7777 \times 4.43 = 3.44$ ml. Hence the calculated absolute temperature corresponding to a fluidity of 200 is

$0.2378 \times 216.5 + 0.6835 \times 305.3 + 0.0787 \times 538.6 = 302.5°$

which is in fair agreement with the value read from the curve of 297.4°.

Ethyl Alcohol and Water Mixtures

We will now take up a case in which the components of the mixture are highly associated. Ethyl alcohol and water are a

particularly good example as there is a very strongly pronounced minimum in the fluidity curves.   The greatest deviation from the linear is in a mixture corresponding to the formula $C_2H_6O.$-$4H_2O$, containing 44.79 per cent alcohol by volume.   To obtain a fluidity of 200, ethyl alcohol requires an absolute temperature of 343.6° and water a temperature of 328.9°, so if there were no chemical change on mixing we should expect a temperature corresponding to the fluidity of 200 in the 44.79 volume per cent
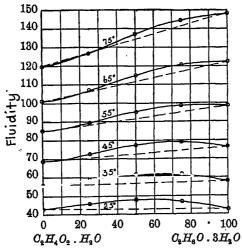
Fɪɢ. 66.—Mixing solutions of ethyl alcohol in water (corresponding to the composition $C_2H_6O.3H_2O$) with solutions of acetic acid in water (corresponding to the composition $C_2H_4O_2.H_2O$) brings about an increase in fluidity.

mixture of $0.4479 \times 343.6 \times 0.5521 \times 328.9 = 335.5°$.   On the other hand, from the constants already given, the temperature required to give the pure hydrate $C_2H_6O.4H_2O$ a fluidity of 200 would be $14 \times 59.2 + 5 \times 24.2 - 2 \times 95.7 = 758.4°$.   But the observed absolute temperature at which the 44.79 volume per cent mixture has a fluidity of 200 is 362.3°.   Hence, if we let x represent the fraction by volume of the mixture combined as $C_2H_6O.4H_2O$, the rest remaining unchanged, we have

$$335.5 (1 - x) + 758.4x = 362.3$$

and $x = 0.0634.$

12

That ethyl alcohol and water are less than 7 per cent combined is surprising in view of the higher amount of combination in chloroform and ether, but the temperature of comparison is very much higher, in the case of water and alcohol being 89°C. But there is another important disturbing factor which must be considered, in that water and alcohol are both highly associated, 2.31 and 1.83 respectively, so that when the two are mixed there is almost certainly dissociation.

That dissociation does occur can be proved as follows: We have seen that when ethyl alcohol and water are mixed there is a lowering of the fluidity. There is also a pronounced lowering of the fluidity when acetic acid and water are mixed. There is furthermore a lowering of the fluidity when acetic acid is mixed with ethyl alcohol. Yet when acetic acid solution ($C_2H_4O_2.H_2O$) is mixed with ethyl alcohol solution ($C_2H_6O.3H_2O$), having practically the same fluidity of 43 absolute units at 25°C, there is a very noticeable increase in the fluidity as seen in Fig. 66 from the paper by Bingham, White, Thomas and Cadwell (1913).

IV. INFLECTION CURVES

The discussion of simultaneous dissociation and chemical combination brings us naturally to the consideration of the fourth type of fluidity-volume concentration curves. There are several pairs of non-aqueous mixtures which fall into this class, such as ethyl alcohol and benzene discovered by Dunstan (1904); but by far more important are certain aqueous solutions of electrolytes, notably the salts of potassium, rubidium, caesium and ammonium. That potassium nitrate added to water lowers the time of flow was discovered by Poiseuille (1847) although priority is usually attributed to Hübener (1873). The list of those substances which lower the viscosity of water has been added to by Sprung (1875), Slotte (1883) and many others and is given in Table XLVI. The phenomenon has been often referred to as "negative viscosity," but since viscosity is a result of friction, which is never negative in fact, the use of the term is not happy. The term "negative curvature," $d^2 \varphi/db^2 < 0$, where b is the volume concentration, is not open to similar objection when discussing the fluidity-volume concentration curves of these solutions.

Apparently all of those aqueous solutions which exhibit negative curvature fall into the class of mixtures showing inflection curves.

TABLE XLVI.—SUBSTANCES WHICH APPEAR TO EXHIBIT THE SO-CALLED "NEGATIVE VISCOSITY" IN AQUEOUS SOLUTION

Substance	Observer
Bromic acid................	Poiseuille (1847)
Hydrobromic acid...........	Poiseuille (1847)
Hydrocyanic acid...........	Poiseuille (1847)
Hydriodic acid..............	Poiseuille (1847
Hydrosulfuric acid..........	Poiseuille (1847
Nitric acid.................	Poiseuille 1847)
Ammonium acetate..........	Poiseuille (1847)
Ammonium bromide........	Sprung (1876)
Ammonium chloride........	Poiseuille (1847)
Ammonium chromate........	Schlie (1869)
Ammonium iodide..........	Hübener 1873), Wagner (1890)
Ammonium nitrate.........	Sprung (1876), Gorke (1905), Walden (1906)
Ammonium thiocyanate......	Sprung (1876)
Caesium chloride...........	Schöttner (1878)
Caesium nitrate............	Brückner (1891)
Ferrous iodide.............	Poiseuille (1847)
Mercuric chloride..........	Poiseuille (1847)
Mercuric cyanide...........	Slotte (1883), Ranken and Taylor (1906)
Potassium bromide.........	Poiseuille (1847)
Potassium chlorate.........	Poiseuille (1847)
Potassium chloride.........	Poiseuille (1847)
Potassium cyanide..........	Poiseuille (1847)
Potassium ferricyanide......	Hübener (1873), Kanitz 1897)
Potassium iodide...........	Poiseuille (1847)
Potassium nitrate..........	Poiseuille (1847)
Potassium thiocyanate......	Sprung (1876), Gorke (1905)
Rubidium bromide.........	Davis, Hughes and Jones (1913)
Rubidium chloride..........	Wagner (1890)
Silver nitrate..............	Poiseuille (1847)
Sodium iodide.............	Poiseuille (1847)
Tetramethylammonium iodide	Schlie (1869)
Thallium nitrate...........	Schottner (1878)
Urea......................	Mützel (1891)

Most workers have confined their attention to dilute solutions and they have studied viscosity relations almost exclusively, so that the positive curvature in concentrated solutions has
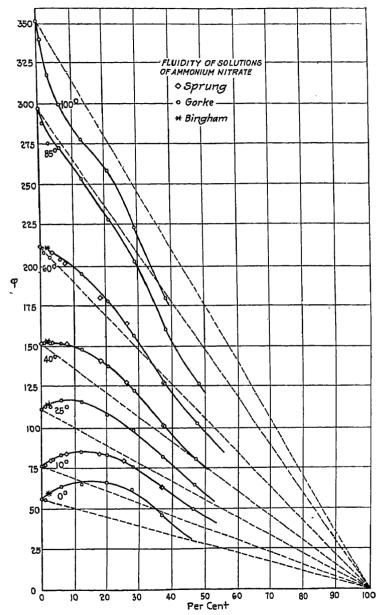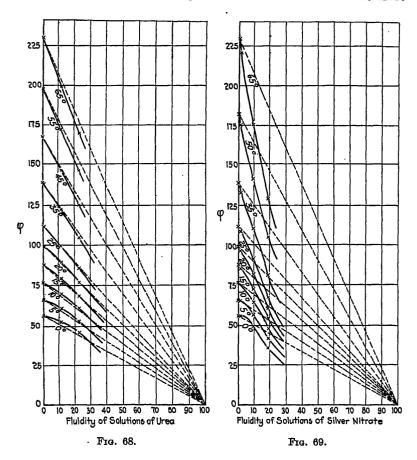
Fig. 67.—Fluidity-volume concentration curves for aqueous solutions of ammonium nitrate, showing both positive and negative curvature.

remained undiscovered. That positive curvature is general even when it is quite unsuspected in dilute solutions is proved by all of the data available, as may be seen by inspection of Figs. 67, 68, 69 and 70. The negative curvature is in each case most

Fig. 68.

Fig. 69.

pronounced at the lowest temperatures and in solutions containing not over 20 per cent of the salt by volume. The negative curvature disappears in concentrated solutions and at high temperatures. If the negative curvature is strongly marked, as with ammonium nitrate or potassium chloride, the positive curvature is unimportant, but when the negative curvature

is weak, as with potassium iodide, silver nitrate and urea, the positive curvature quickly shows itself.

The first important attempt to explain the lowering of the viscosity of water was made by Arrhenius (1887), who thought that it might be due to electrolytic dissociation. Wagner and
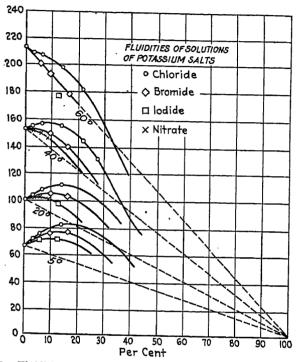
FIG. 70.—Fluidities of potassium halide solutions in water at various temperatures. The curves show negative curvature which is most marked for the chloride, and at low temperatures and at low volume concentrations of the salt. At high concentrations or at high temperatures all of these solutions may show positive curvature, but the nitrate and iodide most readily. (*After Gorke.*)

Mühlenbein (1903), however, showed that the dissociation hypothesis was by itself insufficient as an explanation since salts like $NaNO_3$ and K_2SO_4 are highly ionized and yet do not show negative curvature as does KNO_3. Now that it appears that urea and mercuric chloride solutions both show negative curvature, it would seem probable that electrolytic dissociation is not necessary for the phenomenon. Since these substances in solution are practically unionized.

Jones and Veazey (1907) observed that potassium, rubidium and caesium are the elements with the largest atomic volume and they therefore reasoned that their salts would also be relatively fluid. From what has preceded we are prepared to find relations between fluidity and volume, but as a matter of fact the fluidity of the pure salts in the molten condition is very low. For example, Foussereau (1885) found the fluidity of ammonium nitrate to be 0.505 at 185°C and 0.4037 at 162°C, so that at ordinary temperatures the fluidity of the salt in the undercooled condition would certainly be very low, probably negligible as compared with water. Furthermore, there are salts which show negative curvature but in which the metal has a small atomic volume such as silver nitrate, mercuric chloride, and thallium nitrate. In view of the periodic relationship of the elements, the same coincidence noted by Jones and Veazey would occur with many other properties. Finally there are several salts of potassium and ammonium which have not been found to show negative curvature hence the explanation proposed by Jones and Veazey is not satisfactory.

Explanation of the Inflected Curve

As to the reason for *positive* curvature, it seems probable from what precedes that it is due to combination between the solvent and the solute. That many of the salts of potassium, rubidium, caesium and ammonium exhibit so slight positive curvature is due to their smaller tendency to form hydrates than is usually the case in aqueous solution. In contrast with the salts of potassium, no sodium salts show "negative viscosity." Perhaps the most striking difference between the salts of sodium and potassium, generally so similar, is the greater affinity for water on the part of sodium salts. None of the salts which show negative curvature crystallize from water with water of crystallization, and the few salts of potassium and ammonium which do not show negative curvature do exhibit a tendency to form hydrates. Examples are potassium carbonate, ferrocyanide and sulfate, and ammonium sulfate. It is true that hydrobromic acid solutions are probably hydrated, but according to the measurements of Steele, McIntosh, and Archibald (1906) anhydrous liquid hydrogen bromide has a high fluidity. The small-

ness of the positive curvature is then due to the small amount of hydration which is well-nigh universal in aqueous solution.

The negative curvature, on the other hand, must be due to dissociation either (1) of the salt or (2) of the associated water. Since the negative curvature occurs in dilute solution, the electrolytic dissociation is immediately suggested. If the fluidity of the anhydrous salt in the form of an undercooled liquid is negligibly small, it is hard to conceive of how the dissociation of the salt into two, or at the most a few, ions would increase the fluidity so remarkably, for it must be remembered that there must be a substance present whose fluidity is higher than that of water. Then, as already pointed out, there are substances which give negative curvature which are very *slightly* dissociated into ions, such as urea.

We are then compelled to seek further in our explanation and admit that water itself is dissociated by the presence of the salt or its ions. There is nothing inherently improbable in this since water is highly associated (2.3 at 56°C). The association is less at high temperatures and in concentrated solutions so that under these conditions negative curvature would be less apparent as we have already seen to be the case. It is often assumed that electrolytic dissociation is brought about by union of simple water molecules with the ions of the salt, but if the ions have low fluidity, the fluidity of the solution will evidently not be raised by *uniting* with even *simple* water molecules, hence hydration will not explain the phenomenon. In other words, the formation of larger molecules does not tend to raise the fluidity.

Wagner (1890) has measured the volume of water required to make a liter of normal solution of the chlorides of various salts. In the cases of silver and thallium the nitrates were used instead. Salts like calcium chloride, which unite strongly with water to form hydrates, produce a contraction on going into solution, so that a comparatively large volume of water is required. But rubidium and caesium chlorides expand on going into solution so that the volume of water required is correspondingly small. The difference between the volume of water required and 1 l. is the volume of the salt together with the expansion. Calculating the volume of the salt from its specific gravity the expansion is obtained. The resulting numbers, plotted in curves IV and V in
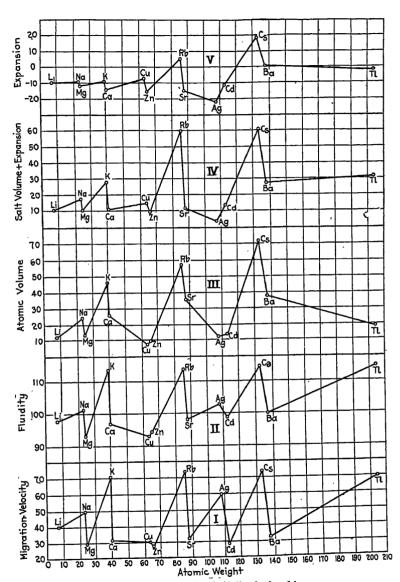
FIG. 71.—Some "periodic" relationships.

Fig. 71, show that in general the salts which occupy the largest volume in solution correspond to those having the highest fluidity curve II, but silver seems to be strongly exceptional. Here again we have evidence that fluidity is proportional to the free volume. The cause of the volume change is also the cause of the negative curvature.

Ammonium iodide according to Getman (1908) and Ranken and Taylor (1906) shows negative curvature but it goes into solution with contraction, according to Schiff and Monsacchi. There is thus a lack of parallelism between the two properties of which one further example may be cited. In ammonium nitrate solutions, the expansion is least in a 7-weight per cent solution and yet the fluidity is a *maximum* in this solution at some temperature between 25 and 40°C. Since we are dealing with inflected curves signifying simultaneous dissociation and chemical combination, these anomalies are to be expected. The limiting volume is continually changing and the specific volume is for that reason no measure of the free volume. There is need for further work in this very important field.

Attempts have been made by Wagner and others to assign to each element a specific viscosity effect in solution. The fluidities of nitrates, chlorides, and sulfates of certain metals in normal solution at 25°C are given in Table XLVII as modified from Wagner. The table shows that the fluidity of the nitrates is

TABLE XLVII.—A COMPARISON OF THE FLUIDITIES OF VARIOUS METALS AND ACID RADICALS IN NORMAL SOLUTION AT 25°C (AFTER WAGNER)

	NO_3	Cl_3	SO_4	$\dfrac{NO_3}{Cl}$	$\dfrac{NO_3}{SO_4}$
K	114.7	113.3	101.2	1.012	1.133
K/H	1.053	1.081	0.974		
H	108.9	104.8	102.5	1.039	1.062
K/Na	1.095	1.112	1.112		
Na	104.7	101.9	91.0	1.027	1.151
K/Zn	1.195	1.199	1.239		
Zn	96.0	94.5	81.7	1.015	1.175
K/Mg	1.201	1.218	1.239		
Mg	95.5	93.0	81.7	1.26	1.169

always higher than that of the chlorides and that of the chlorides is always higher than the fluidity of the corresponding sulphate. The ratio of nitrate to chloride is 1.02 and of nitrate to sulphate 1.14. We may also compare the salts of different metals joined to the same acid radical and thus get a ratio in terms of one metal taken for reference, as potassium. Considering the complex effects due to dissociation, hydration and perhaps other causes, the presence of even imperfect relationships of this kind is remarkable.

CHAPTER VI

FLUIDITY AND DIFFUSION

According to Stokes (1851) a sphere of radius r, impelled through a fluid under a force F, will attain the velocity v

$$v = \frac{F\varphi}{6\pi r} .$$ (62)

This formula is of fundamental importance in the study of the settling of suspensions, diffusion, Brownian movement, the rate of crystallization of solutions, migration velocities and transference numbers of the ions and in the conductivities of solutions.

Settling of Suspensions.—In the case of a falling sphere, the force becomes

$$F = \frac{4}{3} \pi g r^3 (\rho_2 - \rho_1)$$

where ρ_2 and ρ_1 are the densities of the sphere and the medium respectively, so

$$v = \frac{2}{9} g(\rho_2 - \rho_1) r^2 \varphi$$ (63)

This formula enables one to calculate the speed of settling of suspensions. It has been utilized in determining the viscosity of very viscous liquids, *e.g.*, Tammann (1898) and Ladenburg (1907), for determining the radii of the particles in gold suspensions, Pauli (1913), for measuring the charge on the electron in air, Millikan (1910).

The Diffusion Constant.—Sutherland (1905), Einstein (1905) and Smoluchowski (1906) have derived the relation between the diffusion coefficient δ and the fluidity,

$$\delta = \frac{RT}{N} \cdot \frac{\varphi}{6\pi r}$$

where T is the absolute temperature, R is the gas constant (83.2×10^6 c.g.s. units) and N is the number of molecules in a gram molecule (70×10^{22}). The diffusion coefficient is defined as the quantity of solute diffusing per second through a unit cube when the difference in concentration between the two ends of the cube is unity. But Stokes' Law was derived for particles

which are spheres and having a radius large in comparison with the molecules of the solvent. If the particles are so small that the free path a of the molecules of the suspending medium is appreciable in comparison with the radius of the particles, Sutherland (1905), Cunningham (1910) and Millikan (1910) have shown that Stokes' formula becomes

$$\delta = \frac{RT}{N} \cdot \varphi \cdot \frac{1 + \dfrac{Aa}{r}}{6\pi r} \qquad (64)$$

where A is a constant and equal to about 0.815.

The following table from Thovert (1904) indicates that the product of the diffusion constant and the time of efflux is approximately constant for a considerable number of substances.

TABLE XLVIII.—THE RELATION BETWEEN DIFFUSION AND VISCOSITY (THOVERT)

Substance	$\delta \times 10^5$	T, time of efflux	$\delta \times T \times 10^4$
Ether......................	3.10	315	98
Carbon disulfide..............	2.44	405	99
Chloroform...................	1.50	660	99
Mixture ethyl alcohol and ether.	1.51	660	100
Benzene......................	1.24	790	98
Methyl alcohol................	1.16	820	95
Mixture ethyl alcohol and benzene....................	1.03	950	98
Water.......................	0.72	1,330	96
Ethyl alcohol.................	0.59	1,620	96
Turpentine...................	0.48	2,020	97
Amyl alcohol.................	0.155	5,900	92
Glycerol solution.............	0.0104	94,000	98

On the other hand, Oeholm (1913) finds that $\delta\eta$ is not exactly constant for a series of alcohols as compared with water when glycerol is the diffusing substance. Oeholm thinks that association and hydration will account for the variations, at least in part.

Bell and Cameron have applied Poiseuille's formula to diffusion through capillary spaces and find that the distance y which a liquid moves in a given time t is given by the formula $y^n = kt$,

where n and k are constants, and by derivation $n = 2$. The formula is important in dealing with diffusion through porous materials such as soils. But in this type of diffusion, it has often been noticed that there is a separation of the components of the diffusing substances. This subject will come up for consideration later.

Brownian Movement.—Einstein (1906) has shown that the mean square of the projections l of the displacement of the particle in time t on the axis of displacement is

$$l^2 = 2\delta t$$

Substituting into this equation the value of the diffusion, given above

$$l^2 = \frac{RT}{N} \cdot \frac{\varphi t}{3\pi r} \tag{65}$$

This is the equation used by Perrin in his brilliant investigation of the Brownian movement.

The Velocity of Crystallization.—As a crystal forms in a solution, the molecules of the solute are drawn to the growing face of the crystal. The solution bathing the face of the crystal has therefore a lower concentration of solute than the main body of liquid and a process of diffusion must be set up to restore the equilibrium. The rate of crystallization must therefore depend upon the fluidity of the solution. Even in an undercooled liquid, where there is no opportunity for a change in concentration, the viscosity of the liquid retards the proper orientation of the molecules, and crystallization does not take place instantaneously. H. A. Wilson (1900) has demonstrated that the velocity is directly proportional to the fluidity of the liquid at the face of the crystal, according to the formula,

$$v = \alpha(t - t_0)\varphi \tag{66}$$

where v is the velocity of solidification in millimeters per second, α is a constant and t_0 is the temperature at which the velocity of solidification is zero, *i.e.*, the solidifying point, found by extrapolation. This point differs somewhat from the melting-point of the substance, being 37°C for salol instead of 42°C. This signifies that the above relation does not hold when the amount of undercooling, and hence the velocity of solidification, is very small. Since, Tammann has proved that purifying a substance

always diminishes this region of small velocity, Wilson very properly attributes this effect to impurity.

Wilson experimented with salol, benzoic anhydride, benzophenone, and azobenzene confined in long glass tubes of varying diameter. A thermocouple was used to get the temperature of the solidifying surface, which was of course different in tubes of various diameters. How well the observed and calculated velocities of solidification agree can be seen in the following table for salol.

TABLE XLIX.—THE VELOCITY OF CRYSTALLIZATION OF UNDERCOOLED SALOL FROM WILSON, MELTING-POINT, 42.0, $t_0 = 37.0$, $\alpha = 0.065,6$

Temperature, degrees	$t - t_0$	φ	v, calculated	v, observed
35	2	8.77	1.15	1.25
33	4	8.19	2.14	2.5
31	6	7.31	2.90	3.2
29	8	6.49	3.40	3.7
27	10	5.84	3.82	3.9
25	12	5.16	4.05	4.0
21	16	3.90	4.08	4.1
19	18	3.51	4.13	4.1
15	22	2.77	4.00	4.1

Since for all of these liquids the fluidity is as a first approximation a linear function of the temperature, for salol $\varphi = (t - 9.8)$ 2.9, Eq. (66) may be written

$$v = \alpha t^2 - \beta t + \gamma$$

where $\beta = \alpha(9.8 + t_0)$ and $\gamma = 9.8\ \alpha t$. Thus, whereas it is possible to express the velocity of solidification as a function of the temperature only, it is much simpler to express it as a function of the fluidity as was done in Eq. (66).

Migration Velocity, Conductivity and Transference Numbers. That the movement of the ions under the action of electrical attraction should be dependent upon the fluidity of the solution seems a natural inference from what precedes, and a large number of researches have been devoted to the elucidation of the exact relationship. Since the measurement of electrolytic dissociation depends upon this relationship, there can be no question

about its importance.   One has only to compare the migration velocities of a series of ions with the fluidities of their chlorides in normal solution, as shown in curves I and II of Fig. 71 after Bredig, (1894), to see that there is a definite relationship between the two.   In seeking an exact quantitative relationship we are met again by the awkward fact that water is associated and electrolytes in it perhaps always form hydrates, so that an apparently simple aqueous solution is not simple in fact.   The study of molten salts, of liquid metals and alloys, and of non-aqueous solutions for this reason take on a particular importance, but aqueous solutions have naturally received the greatest attention.   The method of investigation is usually to change the fluidity of the liquid by altering the temperature, concentration or pressure and to observe the corresponding change in conductivity.

As early as in 1851 Wiedemann investigated the viscosity and conductivity of various salt solutions of varying concentration. Wiedemann calculated the value of the ratio $m\varphi/\Lambda$, where m is the percentage of salt and Λ the conductivity.   He found that the ratio varies within narrow limits for each salt, $e.g.$, for copper sulfate the value varies from 22.8 to 24.2 when the concentration is increased from 31.17 to 187.02.

Gouré de Villemontée in his monograph on $R\acute{e}sistance$ $\acute{E}lectrique$ et $Fluidit\acute{e}$ has used the results of Bouty and Bender to prove that the ratio $m\varphi/\Lambda$ varies with the temperature in a manner which is the same for all salts. $(Cf.$ Table L.)   We have seen that over a small range of temperature

$$\varphi = \varphi_0(1 + \beta t)$$

so similarly

$$\Lambda = \Lambda_0(1 + \alpha t)$$

where α and β are arbitrary constants and φ_0 and Λ_0 are the fluidity and conductivity at 0°.

Grossman (1883) recalculated the results of Grotrian (1876) and found that the ratio $\dfrac{\varphi}{\Lambda}$ is a constant independent of the temperature, and the temperature coefficients are the same to within 1 per cent.   Bousfield and Lowry (1902) using parabolic formulas, $cf.$ Eq. (53a), in place of the simpler linear ones given above, found that the constants in the two formulas were the same within experimental error.

TABLE L.—THE TEMPERATURE COEFFICIENTS OF FLUIDITY (β) AND
CONDUCTIVITY (α)

Normality	β	α	β/α
Potassium chloride			
3.0	0.0294	0.0230	1.3
2.0	0.0332	0.0259	1.3
1.0	0.0372	0.0291	1.3
0.5	0.0404	0.0302	1.3
Sodium chloride			
3.0	0.0390	0.0279	1.40
2.0	0.0394	0.0290	1.37
1.0	0.0410	0.0292	1.40

TABLE LI.—FLUIDITY AND CONDUCTIVITY OF FUSED SALTS AND SALT
MIXTURES, AFTER FOUSSEREAU

Temperature degrees	φ	Δ	φ/Δ
Sodium nitrate			
305	0.377	0.459	0.821
320	0.439	0.526	0.799
329	0.454	0.555	0.818
340	0.498	0.599	0.832
355	0.561	0.662	0.848
Potassium nitrate			
334	0.545	0.631	0.863
340	0.572	0.661	0.866
358	0.660	0.790	0.835
1 g mol Sodium nitrate + 1 g mol Potassium nitrate			
232	0.248	0.463	0.534
242	0.264	0.502	0.526
266	0.310	0.616	0.504
287	0.361	0.724	0.499
304	0.418	0.791	0.528
313	0.436	0.840	0.519
332	0.532	0.971	0.548
348	0.584	1.123	0.520
359	0.624	1.176	0.530

Foussereau (1885) has examined the changes in fluidity and conductivity of pure water with the temperature and proved that the conductivity is directly proportional to the fluidity. He has also examined several fused salts and salt mixtures and obtained a similar result.   We reproduce in Table LI his results for sodium nitrate, potassium nitrate and an equimolecular mixture of the two salts.   It is to be observed that not only is the ratio different for the different salts but the conductivity is relatively much higher for the mixture than for either of the individual salts.

Völlmer (1894) studied solutions of various salts in methyl and ethyl alcohols and found the temperature coefficients of

TABLE LII.—THE FLUIDITY AND CONDUCTIVITY OF TETRAETHYLAMMONIUM IODIDE AT INFINITE DILUTION IN VARIOUS SOLVENTS AT 0° AND 25°C (AFTER WALDEN)

Solvent	$\varphi^{0°}$	$\Lambda_\infty^{0°}$	φ/Λ_∞	$\varphi^{25°}$	$\Lambda_\infty^{25°}$	φ/Λ_∞
Acetone................	252.0	177.0	1.41	316.0	225.0	1.41
Propionitrile............	185.0	129.0	1.43	242.0	165.0	1.47
Methyl alcohol..........	118.0	90.0	1.31	172.0	124.0	1.39
Ethyl mustard oil........	118.0	82.0	1.44	162.0	106.0	1.53
Acetylacetone...........	87.0	57.0	1.52	128.0	82.0	1.56
Ethyl alcohol............	55.9	37.0	1.51	92.6	60.0	1.54
Benzonitrile.............	51.6	35.5	1.45	80.0	56.5	1.42
Nitrobenzene............	32.6	25.0	1.30	55.0	40.0	1.37

fluidity and conductivity very nearly identical.   Walden (1906) has gone further and proved that φ/Λ_∞ is a constant even when the solvent is varied widely.   He used tetraethylammonium iodide in some forty different organic solvents and found $\varphi/\Lambda_\infty = 1.43$, which is independent both of the nature of the solvent and of the temperature.   A portion of his data will serve to show the nature of the concordance.

These researches all point to the conclusion that Stokes' Law, with a possible correction as already suggested, holds for the diffusion of molecules and ions, so that if a given particle has the same size in different solvents and at different temperatures, the velocity imparted by a constant force will be proportional to the fluidity of the medium.

In ordinary electrolytic solutions, the dissociation is incomplete, hence it is necessary to introduce into our formula the dissociation factor α in order that we may always be dealing with an equivalent number of ions, thus

$$\frac{\alpha\varphi_v}{\Lambda_v} = \frac{\varphi_\infty}{\Lambda_\infty} = \text{const.} \tag{67}$$

where φ_v and Λ_v are the fluidity and conductivity at the volume v. This formula is of use in obtaining the percentage of dissociation by the conductivity method, as indicated by Sutherland (1902) Bousfield (1905) and Pissarevski and Lempke (1905). Working with mixtures of alcohol and water, Doroshevskii and Rozhdestvenskii (1909) found that the ratio $D\varphi/\Lambda$ was a constant over a considerable range of concentrations of alcohol, D being the dielectric constant of the mixture. There is of course a rough proportionality between the dielectric constant and the dissociating power of the solvent.

Hartley, Thomas, and Applebey (1908) have applied the Eq. (67) to solutions of lithium nitrate in mixtures of nicotine and water. These mixtures resemble ethyl alcohol and water in exhibiting a pronounced minimum in fluidity. The coefficient of ionization, calculated by formula (67), shows a maximum. The molecular conductivities of solutions at infinite dilution of the salt show a minimum, closely resembling the fluidity curve, whereas the molecular conductivities of an eighth normal solution show a point of inflection, due to the small ionization in the pure solvent.

Heber Green (1908) has started considerable discussion by the discovery that in water-sucrose mixtures, the conductivity varies, not directly as the fluidity, but

$$\Lambda_\infty = K\varphi^m \tag{68}$$

where $m = 0.70$ for lithium chloride and potassium chloride and 0.55 for hydrochloric acid. In the case of lithium chloride no single value for m can be found which will give entirely satisfactory results. As a matter of fact, Washburn (1911) has found that for the first six sucrose concentrations, a value of m of 0.94 gives better concordance than Green's 0.70. Johnston (1909) has determined the values of m for a number of other solvents using the data of Dutoit and Duperthius (1908) for sodium

iodide solutions, and he finds that in no case does the value of m depart from unity by more than 0.2.

Johnston has calculated the value of m for many cations and anions using different temperatures from 0 to 156°, but found that no single value could be assigned for the hydrogen and hydroxyl ions. The following table will show the nature of his results.

TABLE LIII.—THE RELATION BETWEEN THE CONDUCTANCES AND THE FLUIDITIES OF THE INDIVIDUAL IONS AT DIFFERENT TEMPERATURES C (AFTER JOHNSTON)

Ion	$\Lambda_\infty^{0°}$	m	φ/Λ_∞ 0°	φ/Λ_∞ 100°	φ/Λ_∞ 156°
K............	40.4	0.887	1.39	1.71	1.81
NH_4...........	40.2	0.891	1.40	1.71	1.80
Cl............	41.1	0.88	1.37	1.70	1.81
NO_3..........	40.4	0.807	1.39	1.98	2.19
Na...........	26.0	0.97	2.16	2.27	2.31
½Ca..........	30.0	1.008	1.88	1.84	1.84
$C_2H_3O_2$........	20.3	1.008	2.77	2.73	2.73
½SO_4.........	41.0	0.944	1.36	1.51	1.55
H............	240.0	.....	0.234	0.550	0.741
OH...........	105.0	.....	0.535	0.806	0.971

The slightly hydrated ions K, NH_4, Cl, and NO_3 have a high conductivity and a small value of m, corresponding to an increasing ratio of φ/Λ_∞; the presumably highly hydrated ions Na, ½Ca, $C_2H_3O_2$, and 1/2SO_4 have a low conductivity, a high value of m and a nearly constant ratio of φ/Λ_∞. Hydrogen and hydroxyl are most like the unhydrated group of ions in that they have a very high conductance and a low but rapidly increasing value of φ/Λ_∞.

The explanation of these curious facts is not at hand, but apparently we must assume that the conductivity does vary directly in proportion to the fluidity and seek to explain the inconstancy of the φ/Λ_∞ ratio in the changing solvation of the ions. The phenomenon is as if the unhydrated ions increased in volume with the temperature, whereas the hydrated ions do not.

In the same way the effect of the addition of sucrose to lithium chloride solutions would be explained by an increase in one or both of the ionic volumes due to uniting with the sucrose molecules. That such a hypothesis is not improbable, it is well to add that C. H. Gill has found that sucrose does form crystalline compounds with the halides of sodium and ammonium. He did not find that lithium chloride forms such a compound but there may be a sufficient tendency to unite in solution to explain the effect which seems to be peculiar to sucrose. Glycerol, although highly viscous like sucrose, gives values of m which are unity, according to the determinations of Massoulier (1900) as calculated by Green.

In conclusion, it may be added that there is no connection between the conductivity and the fluidity of a colloidal solution of gelatine, as demonstrated by Griffiths (1896) (see also Lüdeking (1889)). The reason for this peculiarity lies in the heterogeneous character of colloidal solutions as will be more fully discussed later. Schweidler (1895) has also shown that there is no relation between conductivity and fluidity in mercury and certain amalgams.

The Transference Number.—The transport number n_A is expressed by the equation

$$n_A = \frac{\Lambda_A}{\Lambda_A + \Lambda_K}$$

If the equivalent conductances of the different ions change with the fluidity at different rates, the transport number must be also a function of the fluidity. We have the two equations

$$\Lambda_A = \Lambda_{\infty A} \left(\frac{\varphi_v}{\varphi_\infty}\right)^{m_A}$$

and

$$\Lambda_B = \Lambda_{\infty B} \left(\frac{\varphi_v}{\varphi_\infty}\right)^{m_K}$$

whence, according to Washburn (1911)

$$n_A = n_{\infty A} \left(\frac{\varphi_v}{\varphi_\infty}\right)^{m_A - m}$$

where $N_{\infty A}$ is the transport number of the anion at infinite dilution and m is the exponent of Eq. (62) for the salt.

CHAPTER VII

COLLOIDAL SOLUTIONS

If it is highly important to discover the relation between fluidity and conductivity, it is vastly more important to have a solution of the numerous problems in connection with the viscosity of colloidal solutions. Indeed it has been said that the viscometer is to colloid chemistry what the galvanometer is to the subject of electricity, and Graham referred to the viscometer as a *colloidoscope*. Since 1 per cent of colloid like agar agar may give water the properties of a stiff solid, the advantage of employing this property in recognizing the colloid state is clearly apparent.

A pure liquid, at a given temperature and pressure, can have but a single fluidity, but in our study of liquid mixtures we have seen that a mixture of liquids may have an indefinite number of fluidities dependent upon the method of mixing, in other words, upon the structure of the liquid. Since colloidal solutions are always heterogeneous, they always possess structure, and therefore we have this variable always entering into our consideration, whereas heretofore we have given it but scant attention. There is, however, every gradation from a pure liquid, to an incompletely mixed solution, an emulsion, suspension or typical gel.

The Two Types of Colloid Structure.—The structures which may occur are of two kinds, which must be clearly differentiated from each other, because they give rise to phenomena which are in some respects exactly opposite, and this is true in spite of the fact that the two structures may in certain cases merge into each other.

In the one case typified by gelatine, the structure requires time to form and the fluidity at a given moment depends upon the previous history of the solution. When moreover the solution is agitated by shaking or stirring or when it is heated, the structure is damaged and the fluidity is affected. This structure is similar in results to that which would be produced

if an undercooled solution crystallized out needle-shaped crystals throughout the solution so that flow of the resulting mass was stopped except by breaking the crystalline structure. Such a structure is a matter of slow growth, it may be partially destroyed by purely mechanical means, and it arises from forces which are of a polar nature. In view of this analogy we may speak of this type of structure as polar, whereas the second type is non-polar.

In the second type of colloidal solution, typified by clay suspensions those forces are absent which bring about the setting of the gel. We have in the typical case merely particles of suspended solid which affect to some extent the fluidity of the solution, but as we shall see the amount of lowering of the fluidity is very much less than when the structure is polar in character. If the distribution of the particles is uniform, the fluidity of the solution will be independent of time, agitation, and previous treatment.

Suspensions.—For the simplest conceivable case of a solid suspended in a liquid, we can imagine lamellæ of solid parallel to the direction of shear as discussed on page 104. If the alternating lamellæ are sufficiently numerous, the flow will take place without separation of the components, even though the fluidity of the one component is zero. The fluidity of the suspension ϕ is

$$\phi = a\varphi_1 \tag{69}$$

where a is the volume percentage of the medium whose fluidity is φ_1 that is, the fluidity of the medium in the limiting case will be decreased in exactly the ratio which the volume of the solid bears to the total volume of the suspension.

If the lamellæ have an irregular surface, this law becomes invalid. If, for example, the lamellæ are pierced by a number of fine pores, the fluid will fill these pores, yet the stream lines will not pass through the pores or be appreciably distorted by their presence. The fluidity is then

$$\phi = (a - d)\varphi_1 \tag{70}$$

where d is the fraction of the total volume which is pore-space.

The ordinary suspension consists of discrete particles, and for the simplest case we may consider a sphere suspended in a fluid of its own specific gravity. The shearing of the fluid,

which causes any cubical figure of the fluid to assume the form of a rhombohedron, will cause the sphere to rotate, thereby assisting the flow.   The stream lines are curved on account of the presence of the sphere, but the sphere itself moves in a linear direction and with the velocity of the stratum of fluid which would, if continuous, pass through the center of the sphere. Spheres in the same stratum do not approach each other since they all have the same velocity.

Spheres in different strata move with unequal velocity, hence collisions must take place, depending upon the radii of the spheres, their number per unit volume, and also upon any attraction or repulsion which may exist between them.   The
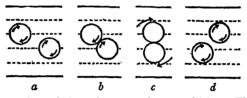
Fig. 72.—Two spheres before, during, and after collision.   The initial rotation of the individual spheres is lost on collision and this results in the dissipation of energy as heat.   In the place of this individual rotation there develops a rotation of the system.   It should be noted that this latter rotation causes the centers of the spheres to move in a transverse direction, indicated by the distances from the dotted lines.

surfaces of two spheres which are approaching each other must be moving in opposite directions, which are at right angles to the line joining their centers, Fig. 72.   The viscous resistance to this shearing action which is set up as they approach will rapidly dissipate as heat their energy of rotation.   In other words, their energy of rotation is converted into heat by the "collision" of the particles.

The contact of two particles, which are large in comparison with molecular dimensions, brings the laws of ordinary friction into play.   The spheres cannot rotate unless the torque exceeds a certain definite value, which will become very important when we come to consider plastic flow.   This value depends upon the pressure existing at their point of contact normal to the surfaces and this pressure in turn depends not only on the rate of shear but on the attraction or repulsion which may exist

between the particles. So when two spheres come into contact, Fig. 72b, they must remain in contact for a definite period unless the spheres are small enough to exhibit Brownian movement. If the spheres were without attraction or repulsion for each other, they would become separated as soon as their centers have come to be in the same vertical plane.

The spheres cannot rotate as individuals during the period of contact until the torque exceeds a certain minimum value. The result is that during the time of contact the group of spheres begin to rotate as a whole, and they pass out of the strata to which they formerly belonged, Fig. 72c, and into layers of different velocities. During this period of acceleration, the liquid will flow around the spheres and through interstices between them. Thus other spheres tend to collide with those already in contact with each other, after which the combined mass tends to rotate as a whole. When equilibrium is reached these clots will have a certain average size, depending upon the number, size, and specific attraction of the particles.

For the present purpose, the important thing to observe is that in the collisions of the particles we have a new source of loss of energy, and if these clots increase in size and number there must come a point when the clots come in contact across the entire width of the passage. At this point viscous flow of the material as a whole stops and plastic flow begins.

For a given substance and volume concentration, the number of collisions will be proportional to the number of particles, which varies inversely as the cube root of the radius. But if the angular velocity is independent of the radius, the energy of rotation will be proportional to the square of the radius, hence the loss of energy, due to collisions will be inversely proportional to the radius. This conclusion, if correct, is very important in indicating that very finely divided particles give comparatively viscous liquids or at higher concentrations plastic solids.

Bingham and Durham (1911) have studied suspensions of infusorial earth, china clay and graphite suspended in water, as well as infusorial earth suspended in alcohol as already referred to on page 54. For each temperature, the fluidity falls off rapidly and linearly with the concentration of solid, so that at no very high concentration by volume the fluidity of zero would be reached, as

shown in Fig. 73, for English china clay and water. This concentration of zero fluidity is independent of the temperature and is the concentration which serves to demarcate viscous from plastic flow.
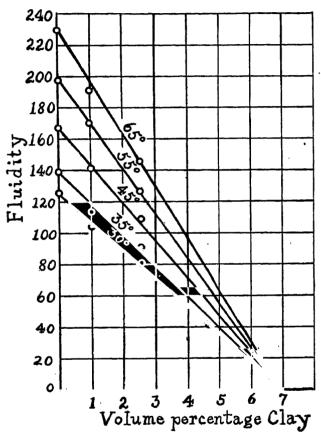
Fig. 73.—The fluidity of aqueous suspensions of clay in water according to measurements of Durham.

We are not to conceive of a suspension of zero fluidity or infinite viscosity as incapable of being deformed, but it would not be permanently deformed by a very small shearing force. It remains an important question which we are unable to answer positively

as yet, whether the viscosity of a suspension is independent of the instrument in which the measurement is made or not. It seems a necessary conclusion that the concentration of zero fluidity must be determined in a long, narrow capillary. The fluidities of suspensions follow the empirical formula

$$\phi = \left(1 - \frac{b}{c}\right)\varphi_1 \tag{71}$$

in which b is the volume concentration of the solid and c is the particular value of b at which the fluidity of the suspension becomes zero. The value of c can vary only from 0 to 1, the value increasing with the size of the particles. This equation closely resembles Eq. (70) and becomes identical with Eq. (69) when $c = 1$.

In Table LIV the fluidities of graphite suspensions are compared

TABLE LIV.—THE FLUIDITIES OF SUSPENSIONS OF GRAPHITE IN WATER AT DIFFERENT TEMPERATURES, (AFTER BINGHAM AND DURHAM)

$c = 5.4$ PER CENT

Temperature, degrees	Volume percentage, graphite	Fluidity observed	Fluidity calculated	Volume percentage, graphite	Fluidity observed	Fluidity calculated
30	0.396	116.8	115.7	1.048	100.9	100.7
35	0.395	129.8	128.3	1.046	113.4	111.7
45	0.394	156.3	154.8	1.042	135.0	134.8
55	0.392	184.9	183.0	1.037	161.7	159.5
65	0.390	215.5	213.1	1.032	192.1	185.7

with the values calculated by formula (71). The two agree extremely well, which may be due to the fact that the graphite suspensions (aquadag) are very stable, obviating trouble due to settling out and clogging the capillary. That the subdivision of the graphite is carried very far is indicated by the very low value of the concentration of zero fluidity, $c = 5.4$ volume per cent.

Some of the suspensions of sulfur by Oden (1912) are plotted in Fig. 74 using volume percentages, taking 1.90 as the specific gravity of sulfur. These values indicate a zero of fluidity at about a 25 volume per cent suspension. Some of the values are not on the curves, particularly at the high concentrations; but the

measurement of the fluidity of suspensions is rendered difficult by the fact that partial clogging of the capillary gives too low fluidities, and settling out of the solid gives too high fluidities. In reference to the discordant observation at 5°C, Oden remarks that the suspension was strongly flocculated.
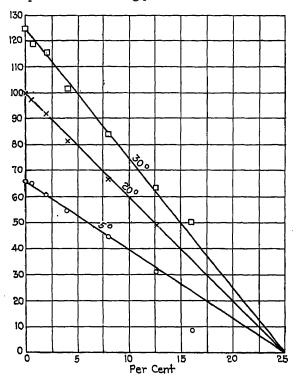
Fɪɢ. 74.—Fluidities of suspensions of sulfur in water at various volume percentages, at 5°, 20°, and 30°C. (*After Oden.*)

It is interesting to find that Trinidad Lake asphalt, treated with benzene gives suspensions which according to measurements of Clifford Richardson (1916) indicate a zero fluidity at 24.6 volume per cent. The fluidities of the suspensions agree well with our formula, which is surprising, since each solution was centrifuged to remove that portion of the suspended matter which would not remain in suspension at that particular concentration.

The curves of infusorial earth in water, page 55, are convex upward at the lower temperatures and convex downward at the higher temperatures. The explanation of this behavior is not known. Plotting the fluidities and concentrations of "night blue" studied by Biltz and Vegesack (1910) we find that all of those curves are convex upward, the zero of fluidity being at

TABLE LV.—FLUIDITIES OF SUSPENSIONS OF TRINIDAD LAKE ASPHALT
IN BENZENE AT ABOUT 20° (AFTER C. RICHARDSON)

Per cent asphalt by weight	Per cent colloid in asphalt	Fluidity observed	Fluidity calculated $c = 34.5$ weight per cent
0	....	153.0	
1	2.54	153.0	149
2	2.01	146.0	144
5	2.09	132.0	131
10	2.73	104.0	109
20	3.13	61.0	64
30	4.19	24.0	20
40	6.51	11.0	13
50	10.69	3.1	

about 9.2 weight per cent. Allowing the suspensions to stand for several days causes a marked decrease in the fluidity as does also the purification of the material.

Woudstra (1908) investigated colloidal silver solutions. In a solution containing only 0.0046 per cent silver by volume, the fluidity at 26° was lowered 4.3 per cent so that it seems possible that a solution containing less than 1 per cent of silver would have zero fluidity! The data are too scanty to permit an exact estimation of the zero fluidity concentration and the fluidity-volume concentration curve is highly convex upward. With the elapse of time and under the influence of electrolytes colloidal silver solutions coagulate and there is a simultaneous increase in the fluidity. This is in accordance with our other knowledge of the effect of size of particle but it is in marked contrast to the effect of "setting" on the fluidity of the polar type of colloids.

Einstein[1] and Hatschek[2] have both considered theoretically the case of suspensions of spherical particles at low concentrations. They both arrive at the formula

$$H = \eta_1 (1 + kb)$$

or

$$\phi = \frac{\varphi_1}{1 + kb} \tag{72}$$

where b is the fraction of solid present by volume and k is a constant for which Hatschek deduced the value of 4.5 and Einstein of 1. The formula is hyperbolic in form while the formula obtained from available experimental material is linear. Their curve is concave upward, and if it held for high concentrations the pure solid would have a fluidity of 18 per cent (Hatschek) to 50 per cent (Einstein) of the fluidity of the continuous medium, which is absurd.

Hatschek states, "It is obvious that the liquid at the upper pole of each spherical particle moves with a somewhat greater velocity than at the lower pole, which is equivalent to a translatory movement of the particles with a velocity equal to half the difference of the two velocities prevailing at the two poles." He thus neglects entirely the rotation of the spheres and assumes that they are moving faster than the stratum of fluid which would pass through their centers. That these two motions are equivalent is at least not self-evident. His formula is obtained by the employment of Stokes' formula for a sphere moving through a viscous medium without rotation.

The view is commonly held that dilute suspensions have a viscosity which is very little different from that of the dispersion medium, but that as the concentration is increased the viscosity suddenly increases. Thus Ostwald in his Kolloid Chemie states, "The curves and tables show that at certain concentrations there is a very sudden increase in viscosity. For silver and glycogen hydrosols these concentrations are respectively about 3.5 and 30 per cent." If the fluidity is in fact linear as we have indicated is the case, the viscosity curve is hyperbolic. There will naturally be a rather sudden increase in viscosity but it has no significance. The question arises, "Does the glycogen *fluidity*-concentration

[1] *Ann. der Physik.*, **19**, 289 (1906).

[2] *Kolloid-Zeitschr.*, **7**, 301 (1901); **8**, 34 (1911); *Trans.* Faraday Soc. (1913).

curve show a sudden drop in fluidity at about 30 per cent?" The glycogen suspensions were studied by Botazzi and d'Errico (1906) using two different viscometers, one from 0 to 20 per cent and the second from 20 per cent on. On plotting the fluidities we find that the values for each viscometer lie on a straight line, but the two lines do not coincide. For the first viscometer, the fluidity of water is 144.0 and the weight concentration of zero fluidity is 27.5, while for the second viscometer it is necessary to assume a fluidity for water of 77.6 and a zero fluidity at 41 per cent concentration. Using formula (64) the calculated values agree well with the observed except at 45 weight per cent which is beyond the concentration corresponding to zero fluidity, as shown in Table LVI. Bottazzi and d'Errico give their viscosities as times of flow, which of course are not proportional to the viscosities, as is so often assumed, so this may perhaps explain the discrepancy between the two viscometers. But more work needs to be done on this subject to definitely establish whether the viscosity of a suspension is independent of the dimensions of the instrument or not. At any rate there is no evidence that the fluidity of concentrated supensions is abnormally low. In fact these experiments lead to the opposite conclusion.

TABLE LVI.—THE FLUIDITIES OF GLYCOGEN SUSPENSIONS AT 37°C (AFTER BOTTAZZI AND D'ERRICO)

Per cent glycogen by weight b	Fluidity observed	Fluidity calculated by formula (71)	
0	144.0	144	Viscometer No. 1
1	138.0	139	$\varphi_1 = 144.0$
5	114.0	118	$c = 27.5$
10	86.0	92	
15	69.0	66	
20	40.0	40	
20	40.0	40	Viscometer No. 2
25	32.0	34	$\varphi_1 = 77.6$
30	20.0	21	$c = 41.0$
35	12.0	11	
40	5.0	2	
45	2.3		

Botazzi and d'Errico obtained the viscosity of glycogen solutions both on raising the temperature and on lowering the temperature to the point of measurement.   The difference was hardly more than the experimental error, which shows that the fluidity of a suspension is not dependent on its past history. This is in marked contrast to the behavior of polar colloids.   On the other hand, non-polar colloids are very susceptible to the effect of electrolytes, even the merest traces often causing a change in fluidity.   As a matter of fact many suspensoids show a slow increase in fluidity on standing, due to the gradual increase in the size of the particles on precipitation, as shown by Woudstra's experiments with colloidal silver suspensions.

Generally speaking, dilute acids and salts with an acid reaction coagulate suspensions and *lower* the fluidity, whereas dilute bases and salts with a basic reaction have a deflocculating action. Neutral salts may act in either way or be without effect.   This is shown in the following table.

TABLE LVII.—THE EFFECT OF ELECTROLYTES ON THE FLUIDITY OF SUSPENSIONS (AFTER BINGHAM AND DURHAM, (1911))

Dispersoid	Concentration dispersoid	Fluidity of suspension	Substance added	Concentration of electrolyte	Fluidity with electrolyte
Infusorial earth....	6.46	62.1	KCl	1:80,000	53.2
Infusorial earth....	6.46	53.2	NaOH	1:20,000	58.3
Graphite..........	0.396	116.8	KCl	1:20,000	116.9
Graphite..........	0.396	116.8	$HC_2H_3O_2$	1:20,000	64.5
China clay........	2.63	41.5	KCl	1:40,000	65.8

The decrease in the fluidity due to acids is attributed to the increase in cohesion between the particles, which results in coagulation.   It is a matter of common experience that acids cause the particles to cohere together and it has already been explained on page 200 how increased cohesion decreases the fluidity.

We need not here discuss the reason why the cohesion of the particles is so much greater in acid solutions, although the subject is one of great interest in the theory of emulsification with its important application in the detergent action of soaps.

Crystalline Liquids.—Reinitzer in 1888 first discovered that

cholesterolbenzoate melts at 145.5° to an opalescent liquid which at 178° became suddenly clear and isotropic. The optical properties of this and other substances of similar behavior was carefully studied by Lehmann. Schenck (1898), Eichwald (1905), Bühner (1906), Bose (1907) and Dickenscheid (1908) have studied
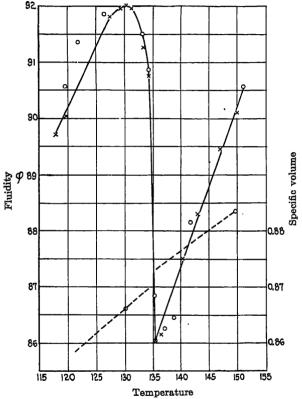
Fig. 75.—Fluidity-temperature curve (continuous) and specific volume-temperature curve (dashed) of *p*-azoxyanisole. (*After Eichwald* (1905) *and Bühner* (1906).)

the viscosities of these substances and shown that these so-called "crystalline liquids" have a higher fluidity than isotropic liquids. The specific volume of crystalline liquids is smaller than that of isotropic liquids of corresponding temperature. In other words, when an anisotropic liquid is heated to the clarifying point, there

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is a sudden increase in volume and decrease in fluidity as shown in Fig. 75 for p-azoxyanisole from the measurements of Eichwald and Bühner. As the temperature is raised, the fluidity increases in a nearly linear manner, passes through a sharp maximum, and suddenly falls to the clarifying point, where there is a discontinuity in the curve. As the temperature is raised still further, the fluidity again increases in a linear manner.

This behavior resembles that of molten sulfur which increases in fluidity up to 150°, where the fluidity is 11.4 according to the measurements of Rotinjanz (1908). It then suddenly falls off to 0.0018 at 180° after which the fluidity gradually increases up to 1.14 at 440°.

Drawing a parallelism between anistropic liquids and molten sulfur, in no way explains the phenomenon, for the behavior of sulfur is unexplained. Bose regards anistropic liquids merely as emulsions of very long life. But an emulsion has invariably a lower fluidity than a homogeneous solution at the same temperature, and according to the theory this must always be the case, so that the emulsion theory seems to be excluded. The phenomenon cannot be accounted for on the basis of the observed volume change, because the volume of the isotropic liquid is greater, which would lead to an increase in the fluidity. We apparently have but one explanation left, *viz.*, that as the anistropic liquid is heated to the clarifying point a new molecular arrangement is formed which has a much larger limiting volume, so that although the molecular volume is increased the free volume is lessened. The same explanation would apply to sulfur.

Emulsions and Emulsion Colloids.—In our discussion of the critical solution temperature, it was made clear that the separation of the components of a mixture in the form of an emulsion is attended by an increase in the viscosity. It seems probable that this increase is due to the viscosities in emulsions being additive, for it follows of necessity that when the viscosities are additive the viscosity will be greater than in a homogeneous mixture of the same composition. As in the case of suspensions, there is considerable evidence that decreasing the size of particle of the disperse phase brings about a corresponding decrease in the fluidity. Martici (1907) experimented with oil-soap emulsions and found that the fluidity becomes less as the drops become

smaller. Buglia (1908) has found that the fluidity of milk is lessened when the milk is "homogenized" by being squirted against an agate plate, thereby increasing the number of fat globules. The apparent decrease in fluidity with emulsification finds excellent practical examples in the manufacture of solid lubricants and of certain household products such as mayonnaise, "whipped cream," and beaten egg albumen. In engine grease less than 1 per cent of water emulsified by means of a solution of soap with mineral oil produces a salve-like grease. Such bodies have the properties of solids and may also be considered in connection with the plasticity of solids.

The question inevitably arises, "How is it possible that water with a high fluidity can decrease the fluidity of a heavy oil, or air decrease the fluidity of albumen, so that the resulting product, emulsion or foam as the case may be, has the rigidity of a solid? To answer this question it is necessary to return to the consideration of our simple case of lamellæ of different liquids at right angles to the direction of shear. The theory that viscosities of emulsions are additive, will account for the fluidity being less than the fluidity of the homogeneous mixture but it will in no way account for the case we have here where the fluidity of the emulsion is less than the fluidity of *either* component.

As the shear progresses, it is to be noted, Fig. 34, that the lamellæ are greatly elongated. But in immiscible liquids this thinning out of the layers is opposed by the surface tension which tends to keep the surface area a minimum. If therefore the shearing force is less than the maximum force arising from the surface tension, continuous deformation will not result. There will be a certain amount of temporary deformation but this too will disappear as soon as the shearing force is removed. In other words, the substance shows not only rigidity but also elasticity; if the shearing force is greater than "the elastic limit," continuous deformation will take place, but since we are dealing with immiscible liquids, the lamellæ will not be thinned out indefinitely, but torn into portions which will gather into drops under the influence of surface tension. Thus in an emulsion, shear tends to make the droplets continually smaller, and consequently to raise the viscosity. This corresponds to the "cold working" of metals. This effect is opposed by the spontaneous coalescence

of the particles on standing, analogous to the "annealing" of metals, so it appears that an equilibrium results and the maximum in viscosity in emulsions may depend upon the rate of shear.

As the lamellæ of the simple case, which we have taken for consideration, are broken up, the viscosities are no longer strictly additive. The droplets become smaller and smaller, the surface tension becomes more and more effective, the droplets become true spheres with an inappreciable amount of flow within the spheres, so that finally the distinction between emulsion and suspension disappears.

We pass finally to that class of polar colloids typified by gelatine, soap and rubber. In some ways they are in sharp contrast with the type which we have just been considering, because their viscosity increases tremendously on standing and decreases as a result of shear, but they are alike in the more fundamental respect of exhibiting the properties of rigidity and elasticity.

It is assumed that the process of gelatinization is the result of polar forces producing a network of crystals or crystal-like material interlacing throughout liquid, without necessarily taking up more than a small portion of the space. The solid network performs the function of the lamellæ at right angles to the direction of shear in our simple case. The cohesion of the solid opposes the shear and gives rise to the rigidity of the gel. The ability of the solid to be deformed without fracture determines its elasticity. This property of elasticity is enormously developed in rubber, and we have seen that it is noticeable in foams and emulsions. Barus (1893) has noted the considerable degree of elasticity in marine glue which may be regarded as a very viscous liquid. It also is of importance in suspensions, as for example in the manufacture of pencils, the "leads" expand considerably, as they are forced out of the die previous to baking.

If gelatinization is analogous to crystallization, we should expect the viscosity to increase on standing and that it would be hastened by "seeding" the solution with a more viscous colloids. We can readily see that shearing the material would result in the destruction of the polar structure of the material and consequently in a decrease in the viscosity. We refer the reader to the rich material furnished by Garrett (1903).

When a hydrogel is exposed to dry air, it loses moisture

and the structure gradually collapses. But showing the properties of a true solid, it remains under tension, and when placed again in water, it swells to approximately its former size, but not indefinitely, as shown by Bancroft.

Increase in concentration of the internal phase very naturally increases the viscosity of the colloidal solution. The addition of non-electrolytes generally affects the viscosity in the way that we would expect from the change produced in the fluidity of the external phase. Since the colloid may unite with the water to form hydrates or with the non-electrolyte, we should expect exceptions to the quantitative application of this rule. Electrolytes have a similar effect on the viscosity of emulsion colloids, potassium nitrate, ammonium nitrate, and potassium chloride which increase the fluidity of water also increase the fluidity of gelatine solution according to the measurements of Schroeder (1903). Sodium sulphate, ammonium sulphate, magnesium sulphate and lithium chloride depress the fluidity. Acids and alkalies however first lower the fluidity and then raise it. For a more adequate account of this complicated subject the reader is referred to the original papers, Schroeder, Pauli, etc.

It has often been a cause for wonder that a gel which has considerable rigidity offers hardly more resistance to diffusion than does pure water. We merely cite the names of Graham (1862), Tietzen-Henning (1888), Voightländer (1889), and Henry and Calugareanu (1901), giving a single observation from Voightländer to the effect that a 1 per cent solution of sodium chloride in a 1, 2, and 3 per cent solution of agar gave a diffusion constant of 1.04, 1.03, and 1.03 respectively. Similarly Lüdeking (1889), Whetham (1896), Levi (1900) Garrett (1903) and Hardy (1907) have found that the conductivity of solutions remains constant during gelatinization.

To understand these peculiarities, it is necessary to consider the phenomenon of seepage of a fluid through a porous material. Suppose, for example, that we consider a single pore; we must assume that since it is a tube of capillary dimensions, the flow must follow the law of Poiseuille and be proportional to the fourth power of the radius of the pore. The question arises, "What will be the effect upon the volume of flow of substituting for the single pore a number of smaller pores whose total pore opening is the

same as that of the single pore?" It is easy to calculate from Poiseuille's law that for a given area of pore opening the volume of flow will be directly proportional to the square of the radius of the individual pores, which are assumed to be alike. If the small pores have a diameter which is only 0.0001 that of the large one, the flow which takes place through the large pore in 1 minute will require about 12 years through the multitude of pores having the same total area. The underlying principle on which the explanation is based is the fact that each layer in viscous flow is carried along by the layer immediately below it, the velocities of the layers increasing in arithmetical progression. The laws of viscous flow are therefore capable of explaining why fluids do not readily flow through jellies and other finely-divided materials.

It is well known that compact clay is almost impervious to both water and oils, and therefore they are often associated, the clay forming an impervious stratum through which the oil or water do not penetrate. The subject of pore openings is therefore fundamentally important to the subject of the circulation of water through soils as well as of their retention of water. The use of compact clay in the cores of dams finds an explanation on this basis.

When it comes to a single particle diffusing through a liquid impelled by electrical attraction or other force, the above considerations no longer hold and the walls of the pores offer no serious resistance, the particle moving through the medium as if it alone were present, without the surrounding network.

THE PLASTICITY OF SOLIDS

Only by the behavior of materials under shearing stresses are we enabled to distinguish between a fluid and a solid. If a body is continuously deformed by a very small shearing stress, it is a liquid; whereas if the deformation stops increasing after a time, the substance is a solid. This distinction is theoretically sharp like the distinction between a liquid and a gas at the critical temperature, but just as a liquid may be made to pass into a gas insensibly, so a solid may grade insensibly into a liquid. Glass and pitch are familiar examples of very viscous liquids. Paint, clay slip, and thin mud in a similar manner must be classed as soft solids. According to the experiments of Bingham and Durham (1911) the concentration in which the fluidity becomes zero under a very small shearing force serves to demarcate the two states of matter.

This simple distinction is not always sharply drawn nor is its significance thoroughly appreciated; and for this reason much labor has been ill-spent in the attempt to measure the viscosity of solids, on the assumption that solids are only very viscous liquids and therefore that plasticity and the fluidity of solids are synonymous terms. The results are unintelligible because the viscosity as so determined in various instruments is widely different.

The views of Clerk Maxwell expressed in his "Theory of Heat" are especially noteworthy and are quoted at length:

"If the form of the body is found to be permanently altered when the stress exceeds a *certain* value, the body is said to be soft or plastic and the state of the body when the alteration is just going to take place is called the limit of perfect elasticity. If the stress, when it is maintained constant, causes a strain or displacement in the body which increases continually with the time, the substance is said to be viscous.

"When this continuous alteration of form is only produced by stresses

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exceeding a certain value, the substance is called a solid, however soft it may be. When the very smallest stress, if continued long enough, will cause a constantly increasing change of form, the body must be regarded as a viscous fluid, however hard it may be.

"Thus a tallow candle is much softer than a stick of sealing wax; but if the candle and the stick of sealing wax are laid horizontally between two supports, the sealing wax will in a few weeks in summer bend under its own weight, while the candle remains straight. The candle is therefore a soft (or plastic) solid, and the sealing wax is a very viscous liquid.

"What is required to alter the form of a soft solid is sufficient force, and this, when applied, produces its effect at once. (This is, of course, only relatively true, because plastic deformation is a function of the time, as will appear later.) In the case of a viscous fluid, it is time which is required, and if enough time is given the very smallest force will produce a sensible effect, such as would be produced by a very large force if suddenly applied.

"Thus a block of pitch may be so hard that you can not make a dent in it with your knuckles; and yet it will, in the course of time, flatten itself out by its own weight and glide down hill like a stream of water."

The italics and parentheses are ours. Butcher (1876) has expressed views quite similar to those of Maxwell.

We may now define plasticity as a property of solids in virtue of which they hold their shape permanently under the action of small shearing stresses but they are readily deformed, worked or molded, under somewhat larger stresses. Plasticity is thus a complex property, made up of two independent factors, which we must evaluate separately.

FIG. 76.—Typical flow-shear diagram for a series of viscous liquids.

Reverting to our fundamental conception of flow between two parallel planes separated by a distance dr and subjected to a shearing force F, we have found that in a viscous fluid

$$dv = \varphi F dr$$

so that if we were to plot the volume of flow through a tube or the rate of shear against the shearing stress, we would obtain

for a series of fluids a family of straight lines passing out from the origin as illustrated in Fig. 76.

'In a plastic solid, a certain portion of the shearing force is used up in overcoming the *internal friction* of the material. If the stress is just equal to the friction or yield value, the material may be said to be at its elastic limit. If the stress is greater than the friction f, the excess, $F - f$, will be used up in producing plastic flow according to the formula

$$dv = \mu \; (F - f) \; dr \qquad (73)$$

where μ is a constant which we will call the *coefficient of mobility*
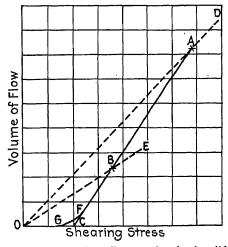
FIG. 77.—Flow-shear diagram of a plastic solid.

in analogy to the fluidity of liquids and gases. If we were to plot the volume of flow against the shearing stress we would again obtain a straight line for a given material but it would not pass through the origin, ABC Fig. 77.

It is easy now to see why the "viscosity" of plastic substances, as measured in the usual way for liquids, is not a constant. Referring to the figure, if we take two determinations of the flow A and B, we see that they correspond to entirely different viscosity curves OD and OE.

When the stress is not equal to the yield value, the material undergoes elastic deformation and an opposing force arises

which would restore the body to its original shape if it were perfectly elastic, as soon as the stress was removed. On the application of the stress, the restoring force is first zero, then gradually increases to a maximum, when at last the flow causes the strain to disappear as fast as it is produced.

The elasticity e of a solid may be calculated, according to Morris-Airey (1905), from the fundamental formula

$$ds = eFdr \qquad (74)$$

where ds is the distance which one plane of the material is sheared in reference to another plane which is separated from it by a distance dr, each being subject to the shearing force F. Morris-Airey has applied this formula to tubes of circular cross-section filled with gelatine and obtained the rigidity[1] ζ which is the reciprocal of the elasticity

$$\zeta = \frac{\pi g R^4 P}{8 V l} \qquad (75)$$

where V is the volume of the temporary deformation. It is assumed that the solid is incompressible. The analogy of this formula with that of Poisuille is striking.

The Methods for Measuring the Friction and Mobility

To determine the two quantities, friction and mobility, which go to make up the plasticity of a material, *i.e.*, to locate the curve in Fig. 77, it is necessary to make at least two measurements of the flow, using different stresses. We may use the tube method (Bingham (1916)), the torsion method (Perrott (1919)), or we may observe the flow in a rod under traction or torsion, the flow of a cylinder under axial compression, the rate of bending of a horizontal beam of the material under its own weight, or the flow of a freely descending stream of material, (Trouton and Andrews (1904)). Still other methods have been suggested such as the rate of decay of vibrations in solid bodies, (Kelvin (1865) and others).

The friction is most easily obtained by the graphical method, plotting the rates of flow V/t, against the shear, $F = \dfrac{PR}{2l}$ and

[1] The assumption which is sometimes made that the rigidity is the reciprocal of the mobility is incorrect.

extrapolating the curve to the axis; the value of the intercept will evidently be the friction. We may also use the algebraical method. In either case at least two measurements of the rate of flow $V_1/t_1 = v_1$ and $V_2/t_2 = v_2$ are necessary corresponding to
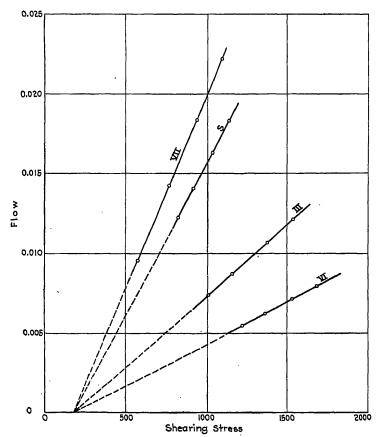
FIG. 78.—Flow-shear curves of a certain paint, using capillaries of varying length and radius.

the shears F_1 and F_2, respectively. Assuming that the mobility is independent of the rate of flow, Eq. (73) integrated in Eq. (89) gives us

$$f = \frac{v_2 F_1 - v_1 F_2}{v_2 - v_1} \tag{76}$$

The following table, taken from the work of Bingham and Green on paints, proves the validity of the general law of plastic flow expressed in Eq. (73).　The friction, when expressed in terms of shear—and not in terms of pressure—is nearly constant and not a function of the dimensions of the capillary.　It is a fact, however, that the rate of flow is not directly proportional to the shear, when the shear is too small, but when the shear is sufficiently high the relation becomes linear, as is proved by plotting
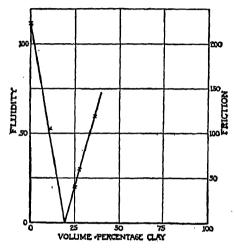
Fig. 79.—The relation of fluidity and friction to volume concentration of solid in clay suspensions.

the values in the table, Fig. 78.　The table also indicates that the mobility is a constant independent of the rate of flow or of the dimensions of the capillary.　The reason for the rate of flow-shear curve not being linear as the rate of flow is decreased will be considered when we come to discuss the theory of plastic flow.

By measuring the fluidity of suspensions containing increasing amounts of solid in suspension, Bingham and Durham found it possible to obtain a concentration which would possess zero fluidity when the shear was very small.　Conversely, by measuring the friction of suspensions containing decreasing amounts of solid, it is possible to find a concentration which would have

zero friction, Fig. 79. Evidently these two concentrations are identical, and the concentration of zero fluidity or of zero friction is a fundamental constant of the material giving important information in regard to its nature, it being intimately related to the size of the particles and to the adhesion between them.

The flow of a given material is defined completely by a knowledge of the friction and mobility, but when the concentration of the suspension is changed, a knowledge of the concentration of zero fluidity is necessary in order to estimate the effect produced
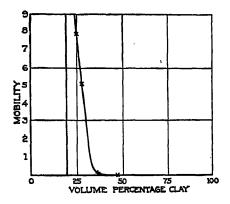
Fig. 80.—Relation between mobility and volume concentration of solid in clay suspensions.

upon the friction and mobility. It therefore seems probable that the concentration of zero fluidity is a variable which is independent of both the friction and the mobility.

Finally, we may add that the mobility of suspensions decreases very rapidly with increasing concentration of solid as indicated by measurements of the author which are plotted in Fig. 80. Clay suspensions were used having a concentration of zero fluidity of 19 per cent by volume. The mobility starts at a very large but undetermined value and quickly falls to a very small value in a concentration of about 50 per cent by volume. The friction on the other hand, starts at zero in the 19 per cent mixture and rises steadily and in an apparently linear manner as the concentration is increased as seen in Fig. 79.

TABLE LVIII.—FRICTION AND MOBILITY OF A PAINT AS MEASURED BY BINGHAM AND GREEN[1]

Number of observation	V–t centimeters per second	Pressure grams per square centimeter	$F = \dfrac{FR}{2l}$ dynes per square centimeter	f dynes per square centimeter	$F-f$	μ	Remarks	Observations used in calculations
1	0.0005836	670.8	1030.7	98.2	938.7	0.260	Capillary 8	1 and 2
2	0.0004557	537.8	826.3	84.6	734.3	0.260	$r = 0.014486$ cm	2 and 3
3	0.0003344	409.3	628.9	75.9	536.9	0.261	$l = 4.620$ cm	3 and 4
4	0.0002133	277.5	426.4	[66.0]	334.4	0.267		4 and 5
5	0.0001661	225.6	346.6	[57.7]	254.6	0.273		5 and 6
6	0.0001019	152.9	234.9					
7	0.002424	670.2	1458.6	101.0	1366.6	0.253	Capillary VI	
8	0.001912	538.5	1171.9	85.4	1079.9	0.254	$r = 0.020805$	
9	0.001418	409.5	891.2	87.5	799.2	0.255	$l = 4.684$ cm	9 and 10
10	0.0008987	274.3	596.9	[55.6]	504.9	0.256		10 and 11
11	0.0004164	143.3	311.8	[53.7]	219.8	0.272		11 and 12
12	0.0002880	106.7	232.2					
13	0.004638	671.7	1723.0	81.6	1631.0	0.246	Capillary III	13 and 14
14	0.003678	539.1	1382.9	93.2	1290.9	0.246	$r = 0.02450$	14 and 15
15	0.002726	409.0	1049.2	85.1	957.2	0.246	$l = 4.681$ cm	15 and 16
16	0.001758	275.6	706.9	[75.1]	614.9	0.247		16 and 17
17	0.0008267	145.1	372.2	[63.5]	280.2	0.255		17 and 18
18	0.0005856	110.0	282.2					

The average friction used in calculating the mobility is 92.0 dynes per square centimeter, which gives an average mobility of 0.257. When the rate of flow V/t is too small, the friction becomes smaller, as seen in the table and the last two values for each capillary may well be neglected.

The Capillary Tube Method.—Unless the conditions of flow are carefully chosen, the friction constant does not manifest itself, or at any rate the amount of shear is not a linear function of the shearing stress. This departure from linearity is very often shown at the low rates of shear as indicated in Fig. 76 by the curve *FG*.

This peculiarity is not fully understood at present and the worker will do well to avoid anxiety in regard to it by choosing the conditions as nearly ideal as possible so that the flow will be a linear function of the shearing stress.

Nevertheless the cause of the above peculiarity must be investigated in detail if we are to understand fully the nature

[1]*Proc.* Am. Soc. for Test. Mats. (1919).

of plastic flow and it has already had the attention of Buckingham (1921). In plastic material confined between two parallel planes of indefinite extent which are being sheared over each other, the shearing stress F will be identical at every point. But in flow through a capillary tube according to Buckingham this is not the case; the shear increases continually from the center of the capillary outward and only at a certain distance r_o does the shearing force become sufficient to overcome the friction. Therefore the material at the center of the capillary moves as a solid plug with the velocity v_o, and beyond the radius r_o the material moves in telescoping layers. This results in the flow not being a linear function of the pressure.

But there are other possible causes of the peculiarity which may be mentioned here. The plastic material next to the wall may have a lower concentration of solid than elsewhere resulting in apparent *slippage*. Or the shearing stress may cause the liquid to flow between the particles of solid, *seepage*.

Buckingham suggests that the friction between the particles during flow may not be the same as the static friction. It seems further possible that the friction will need further definition when the individual particles of the plastic material are of very different sizes. We shall at first assume that slippage and seepage are both absent and that the particles of solid are uniformly small.

The total force producing the flow through a capillary tube is $\pi P R^2$ and since there is no acceleration, this is opposed by a force in the opposite direction $2\pi R l F$. If p is the pressure which is used up during the flow in overcoming the friction, the friction f is defined by the equation

$$f = \frac{R}{2l}p \tag{77}$$

It also follows that

$$f = \frac{r_0}{2l}P \tag{78}$$

$$F = \frac{R}{2l}P \tag{79}$$

Since the speed decreases as the radius increases, Eq. (73) becomes

$$dv = -\mu\left(\frac{Pr}{2l} - f\right)dr \tag{80}$$

where v is the velocity parallel to the axis at the radius r. The speed of the material in the variable region is obtained by integrating Eq. (80) from $r = R$ to $r = r$ or

$$U_r = -\mu \int_R^r \left(\frac{Pr}{2l} - f\right) dr = \mu \left[\frac{Pr^2}{4l} - fr\right]_r^R$$

$$= \mu \left[\frac{P}{4l}(R^2 - r^2) - f(R - r)\right] \qquad (81)$$

The speed of the solid plug is obtained by making $r = r_0$ in Eq. (81), and is after simplifying

$$U_0 = \mu \left(\frac{PR^2}{4l} + \frac{lf^2}{P} - fR\right) \qquad (82)$$

The volume of flow per unit of time is V/t and

$$\frac{V}{t} = \int_0^R 2\pi r v\, dr$$

or using Eqs. (81) and (82)

$$\frac{V}{t} = \pi r_0^2 v_0 + 2\pi \int_{r_0}^R r v_r\, dr. \qquad (83)$$

But from Eqs. (78) and (82)

$$\pi r_0^2 V_0 = \pi \mu \frac{4l^2 f^2}{P^2}\left(\frac{PR^2}{4l} + \frac{lf^2}{P} - fR\right)$$

and from Eq. (81)

$$2\pi \int_{r_0}^R r v_r\, dr = 2\pi \mu \int_{r_0}^R \left[\frac{P}{4l}(R^2 r - r^3) - f(Rr - r^2)\right] dr$$

$$= 2\pi \mu \left[\frac{R^4 P}{16l} - \frac{R^3 f}{6} - \frac{P}{4l}\left(R^2 \frac{r_0^2}{2} - \frac{r_0^4}{4}\right) + f\left(R\frac{r_0^2}{2} - \frac{r_0^3}{3}\right)\right]. \qquad (84)$$

and introducing the value of r_0 from Eq. (78), we have

$$= 2\pi \mu \left(\frac{R^4 P}{16l} - \frac{R^3 f}{6} - \frac{R^2 lf^2}{2P} + \frac{2Rl^2 f^3}{P^2} - \frac{5}{3}\frac{l^3 f^4}{P^3}\right). \qquad (85)$$

Introducing these values of the separate terms of Eq. (83) and simplifying, Eq. (83) becomes

$$\frac{V}{t} = \pi \mu \left(\frac{R^4 P}{8l} - \frac{R^3 f}{3} + \frac{2l^3 f^4}{3P^3}\right)$$

or

$$\frac{V}{t} = \frac{\pi \mu R^4}{8l}\left[P - \frac{4}{3}\left(\frac{2lf}{R}\right) - \frac{1}{3P^3}\left(\frac{2lf}{R}\right)^4\right]$$

and now introducing the value of p given by Eq. (77),

$$\frac{V}{t} = \frac{\pi \mu R^4}{8l}\left(P - \frac{4}{3}p + \frac{p^4}{3P^3}\right). \qquad (86)$$

For large values of the applied pressure, the last term of Eq. (86) becomes very small and the curve becomes very nearly linear and coincident with its asymptote

$$\frac{V}{t} = \frac{\pi\mu R^4}{8l}\left(P - \frac{4}{3}p\right) \tag{87}$$

or

$$= \frac{\pi\mu R^3}{4}\left(F - \frac{4}{3}f\right). \tag{88}$$

The curve rises above the asymptote as the applied pressure becomes very small, but it crosses the pressure (or shearing stress) axis when $P = p$ (or $F = f$). On differentiating Eq. (86) in respect to the pressure one finds that the slope of the curve vanishes when $P = p$, hence the curve is tangent to the axis.

The intercept of the asymptote is thus 4/3 of the true friction which would be obtained by other methods as, for example, plastic material confined between parallel planes which are being sheared over each other. If in practice conditions may be controlled so that all of the observed points lie on a straight line, it will mean that the flow is taking place practically throughout the capillary in telescoping layers, the term $p/3P^3$ being negligible.

Were we to assume that the material throughout the capillary flows in telescoping layers for all shearing stresses above f, we will obtain

$$\frac{V}{t} = \pi\int_o^R r^2 dv = \frac{\pi\mu\,(P-p)}{2l}\int_o^R r^3 dr = \frac{\pi\mu\,(P-p)R^4}{8l}$$
$$\frac{V}{t} = \frac{\pi\mu R^3}{4}\,(F-f) \tag{89}$$

which differs from Eq. (88) in having f in place of 4/3f. It is highly desirable that some one measure the friction both by the capillary tube method and other methods using a given material, to make sure that they give identical values for the friction.

Not being able to reproduce satisfactorily the data of Bingham and Green, Buckingham has attempted to allow for slippage. If there is a thin layer of viscous liquid of thickness e separating the plastic material from the wall, it will increase the velocity of the plastic material by the amount $e\varphi F$, hence the increase in the volume of flow per unit of time over that given by Eq. (88) is $\pi R^2 e\varphi F$ approximately. But at present it is not certain that there is slippage after the flow is established by increasing the shearing

stress somewhat above the friction, so we have no idea as to how the value of e may vary with the rate of shear, and the equation becomes unmanageable. Fortunately by using the higher rates of shear we can apparently always obtain the simple linear relationship. If later experiments prove that this is not the case it will be time to use the more complex formulas.

The Traction Method.—Trouton has discovered that the rate of flow in a rod of material subjected to traction is not proportional to the tractive force T, but analogously to Eq. (73)

$$dv = \lambda(T - t)dr \qquad (90)$$

where λ is the coefficient of plastic traction, and t is a tractive friction constant. The value of t may be found by plotting the elongation dv/dr against the tractive force and extrapolating the curve to the axis. Trouton has obtained values of λ for pitch of 2.3×10^{-10} and for shoemakers' wax of 1.7×10^{-7}. To obtain the relation between the coefficient of plastic traction and the mobility, we note that the tractional force applied to a rod may be resolved into two equal shearing stresses at right angles to each other and at 45° to the direction of traction. The value of either shearing stress is one-third of that of the tractive stress, hence the *friction* is one-third of the tractive friction and the *mobility* is one-third of the plastic traction coefficient as shown in Table LX.

The Torsion Method.—Trouton applied a constant torque to the ends of a cylinder or tube of substance and observed the relative motion of the ends. He found that rods which were carefully made could be twisted almost indefinitely, provided that they were maintained in a horizontal position. The motion was fastest when the stress was first applied but the angle of twist per unit length U soon became a linear function of the time. Conversely when the stress was removed, the bar started to twist in the opposite direction. He made the experiment of removing weights at such a rate that the rod would not move in either direction, and found that the weights remaining were inversely proportional to the time elasped. This kind of elastic recovery was found to be present in glass and sodium stearate. Trouton does not seem to regard his materials as solids but he makes it very clear that the angular velocity is not directly pro-

portional to the torque, and there is a very considerable magnitude to the value which can be assigned to the friction in his experiments with pitch.

Trouton assumes from symmetry that any two planes in the material, lying at right angles to the axis of the cylinder, move over each other, about the common axis, remaining plane all the while.

Let δx be the distance apart of the two planes, and $\delta\omega$ be the relative angular velocity of the planes, then

$$F - f = \frac{2\pi}{\mu} \; \frac{\delta\omega}{\delta x} \int_o^R r^3 dr$$

where F is the torque applied and f is the force used up in overcoming the friction, obtained by extrapolation.

Thus for a solid cylinder we have

$$\mu = \frac{\pi U R^4}{2(F-f)} \tag{91}$$

and for a tube of material this becomes

$$\mu = \frac{\pi U (R_1{}^4 - R_2{}^4)}{2(F-f)} \tag{92}$$

where R_1 and R_2 are the external and internal radii respectively.

Trouton proved the validity of the fourth-power law by using two cylinders of pitch whose radii were 0.36 and 0.67 cm and obtained mobilities of 1.01×10^{-11} and 0.99×10^{-11} respectively which is excellent agreement.

The Sagging Beam Method.—The rate of sagging U of a rod at its center is found to be

$$U = \frac{5}{384} \; \frac{gmL^4}{\lambda I} \tag{93}$$

where m is the mass of the rod between the supports, L is its length and I is the moment of inertia of the cross-section of the rod, and g is the gravitation constant. This does not take account of the friction.

In order to prove that the rate of sagging of a beam varies as the fourth power of the length, Trouton measured the times T which beams of different lengths required to sag a certain distance. Table LIX shows that TL^4 is very nearly constant.

TABLE LIX.—EXPERIMENTS ON THE SAGGING OF A ROD OF PITCH AT 15°,
DEMONSTRATING THAT THE TIME T REQUIRED TO SAG A GIVEN DIS-
TANCE VARIES INVERSELY AS THE FOURTH POWER OF THE DISTANCE
L BETWEEN THE SUPPORTS (AFTER TROUTON)

L	T	TL^4
33	14.6	1.7×10^7
30	18.5	1.5
27	30.4	1.6
24	47.0	1.6

That the different methods agree with each other is shown
in Table LX.

TABLE LX.—A COMPARISON OF THE COEFFICIENTS OF PLASTIC TRACTION
AND MOBILITY AS DETERMINED BY VARIOUS METHODS (AFTER TROUTON)

Substance	λ	Method	u	Method	μ/λ
Pitch I	2.3×10^{-11}	Traction....	7.1×10^{-11}	Torsion,.	3.07
Pitch II	2.8×10^{-11}	Traction....	1.0×10^{-10}	Torsion...	3.60
Pitch II	3.0×10^{-11}	Sagging.....	....	....	3.30
Pitch and tar I	7.8×10^{-9}	Traction....	2.4×10^{-10}	Torsion..	3.07
Pitch and tar II	1.5×10^{-10}	Traction....	4.5×10^{-10}	Torsion...	3.04
Shoemaker's wax	1.9×10^{-7}	Traction....	5.0×10^{-7}	Torsion..	2.95
Pitch and tar 3:1 III	1.3×10^{-5}	Sagging.....	3.8×10^{-5}	Efflux....	3.25
Pitch and tar 3:1 IV	1.1×10^{-5}	Descending column.....	3.6×10^{-5}	Efflux....	2.91

THE THEORY OF PLASTIC FLOW

A plastic solid is made up of particles which touch each other
at certain points. The spaces between the particles may be
empty or it may be filled with gas, liquid, or amorphous solid.
Flow necessitates the sliding of these particles the one over the
other according to the ordinary laws of friction, so long as the
particles are large enough so that their Brownian movement is
negligible. It is by no means necessary that the particles be
touching at the maximum number of points, corresponding to
"close-packing." As a matter of fact, close-packing of the
particles prevents flow from taking place. It is merely necessary
that the particles touching each other form arches capable of
carrying the load, as already indicated on page 201. It is evident

that as aggregates of particles are formed in the process of collisions, and the size of these aggregates increases as the concentration of solid increases, there must come a time when such aggregates or clots will touch each other and form an arch or bridge across the space through which the flow is taking place. At that concentration the friction will have a finite value, and the material may be said to have a structure just as was the case of the jelly or foam already considered.

The pore space may vary between very wide limits, but if the suspended particles are assumed to be uniform spheres, it can easily be calculated that cubical close-packing, would leave a pore space of $1 - \pi/6$ or 47.64 per cent by volume, irrespective of the size of the particles. It is possible to get the particles still closer together until with tetrahedral close-packing, which we have in a pile of cannon-balls, the pore space is $1 - \pi/3\sqrt{2}$ or 25.96 per cent by volume, but in this case the particles are interlocked and no true flow is possible but *rupture,* with disintegration of the particles. When the pore space is roughly 50 per cent, the mobility is zero, and it is only as the pore space is in excess of this figure that the mobility has a finite value. This excess pore space thus plays a rôle which is analogous to the free volume of liquids.

As there is a minimum in the allowable pore space in a plastic solid, so there is a maximum, for as the pore space increases the substance finally ceases to become a solid. This concentration of zero friction was found for a certain English china clay to be 19.5 per cent by volume when suspended in water containing one-tenth of 1 per cent of potassium carbonate. If the particles of clay were spheres of uniform size, suspensions of this material would show plasticity in concentrations of solid from 19.5 to 47.64, *i.e.,* over a range of roughly 30 per cent. Colloidal graphite exhibits zero fluidity when there is only 5.4 per cent in suspension, hence it has a plasticity range of concentrations of over 40 per cent. On the other hand, suspensions of many coarse materials have a plasticity range which is much constricted, which for practical purposes, is sometimes a serious disadvantage.

There is abundant evidence that as the diameter of the particles is decreased, the opportunity for the particles touching

is increased, which enhances the friction, but this effect reaches a limit eventually when the particles are so small that their Brownian movement becomes appreciable and strains in the material are not permanent.

If, as we have intimated, the friction is subject to the laws of ordinary external friction, the friction should be closely dependent upon the adhesion of the particles to each other but independent upon the nature of the medium so long as it is inert. In confirmation of this we note that whereas the china clay referred to above showed zero friction when the volume concentration was 19.5 per cent, the same clay thoroughly shaken down in a measuring flask in the dry state showed a pore space of 18.4 per cent, the pore space in this case being filled with air. The two values are in very close agreement. Infusorial earth exhibited zero fluidity in water when present to the extent of 12.9 per cent by volume, whereas in ethyl alcohol the corresponding concentration was 12.1 per cent. Finally it has been observed that the temperature and therefore the fluidity of the medium is without effect upon the friction.

Adhesion between the particles may be influenced in a marked degree by the addition of small amounts of substances of the most diverse character. Generally speaking, substances which yield hydrogen ions increase the adhesion, *i.e.*, promote flocculation, while substances which yield hydroxyl ions decrease the adhesion and promote deflocculation. Colloids also have a noteworthy effect. In flocculation, structure is produced and therefore the friction is enhanced. In a given instance, using 50 per cent china clay in water, the friction was lowered from 78 to 59.5 by adding merely one-tenth of 1 per cent of potassium carbonate, which of course yields hydroxyl ions.

The mobility is dependent upon the fluidity of the medium. This in turn is influenced by the temperature, hence we may expect that the mobility of a solid will be dependent upon the temperature. Thus in a 50 per cent clay suspension the mobility at 25° was found to be 5.11 and at 40°, 7.88. The ratio between these mobilities is 1.54 which is very close to the ratio of the fluidities of water at these two temperatures

$$\frac{\varphi^{40°}}{\varphi^{25°}} = \frac{166.9}{111.7} = 1.49.$$

The result of deflocculation is to greatly increase the mobility. Thus one-tenth of 1 per cent of potassium carbonate raised the mobility from 1.17 to 5.11 which is an increase of over 330 per cent, a truly remarkable effect.

SEEPAGE AND SLIPPAGE

When the shearing force is just a little less than the friction, there is generally a certain amount of flow which is due to two different causes. In the first place, under ordinary conditions of flow the pressure tends to cause the medium to seep through the material. With this filtration phenomenon there is a local change in concentration and therefore a change in the character of the flow. Seepage is unimportant when the medium is viscous and the suspended particles are small as in paint.

The second difficulty is due to slippage, which comes from lack of sufficient adhesion between the material and the shearing surface. The shearing surface is wet with the liquid medium and the smooth surface affords little opportunity for the attachment or interlocking of the particles. The result is that there is a layer of liquid between the shearing surface and the main body of the suspension and flow takes place in this layer according to the laws of viscous rather than plastic flow. Green (1920) has observed this phenomenon in paint under the microscope, the material moving as a solid rod until the shear reaches a certain value when it begins to move in telescoping layers. This slippage causes the rate of flow-shear curve to be no longer linear when the rate of flow is small and the curve passes through the origin.

Difficulties due to seepage and slippage can be overcome by using sufficiently high pressures, so that the viscous flow factor will become negligible. In this case there should be a linear relation between shear and rate of flow.

HYDRAULIC FLOW AND THE PLASTIC STATE

So far as known to the author, no one has yet used rates of flow high enough to bring about eddy currents, which are so troublesome in the case of liquids. But there is the same necessity for using long narrow tubes for measuring the flow,

rather than orifices or very short tubes, for the flow of a plastic material through an orifice gives no idea of the mobility of the material, just as the flow of a liquid through an orifice is largely independent of the viscosity of the liquid. Flow through an
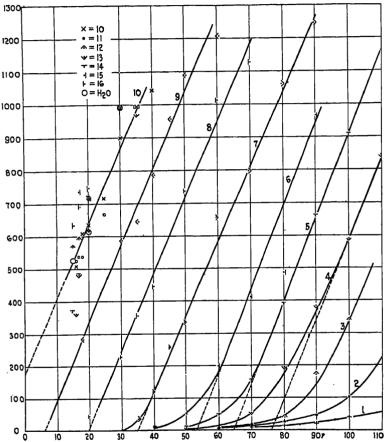
Fig. 81.—Hydraulic flow of a plastic material after experiments of Simonis.

orifice does, however, lead to a knowledge of the friction constant of the plastic substance, as proved by the experiments of Simonis (1905).

Simonis used 40 g of Zettlitz earth with 100 g of water to which were added successive portions of a dilute solution of

sodium hydroxide containing 1.795 g per liter. The pressure seems to have been measured as centimeters of water head, and the volume of flow in milliliters per 600 sec. He measured the flow of 16 mixtures and pure water, designated by the numbers on the curves in Fig. 81. The amounts of sodium hydroxide solution added are noted in the second column of Table LXI.

The curves are nearly linear except when the volume of flow is small. The curvature is probably due to seepage. The horizontal distance of the different curves from the curve No. 10 is evidently a relative measure of the friction constant. The values of the friction constant f as obtained graphically are given in the table. We have found that it is possible to calculate this relative friction constant f' by means of the formula

$$f' = 154 - 14.1c \tag{94}$$

where c represents the number of milliters of sodium hydroxide added. It appears, therefore, from a comparison of the values of f and f' that Simonis' experiments confirm our conclusion that the friction is a linear function of the concentration. We note that the friction constant continually decreases as water is added until 11 ml have been added after which further additions are without effect upon the rate of flow. On adding 11 ml, the material reaches the concentration of zero fluidity or zero friction, and the curve 10 should pass through the origin. That the curves 10 to 17 all coincide with curve 10 accords with what we should expect of liquids flowing through an orifice.

The fact that all of the curves are sensibly parallel constitutes the remarkable difference between flow through a capillary and flow through an orifice. It does not signify that the plastic mixtures all have the same mobility any more than it signifies that all of the liquid mixtures have the same fluidity. It means simply that the rate of flow through an orifice is independent of the fluidity or mobility. If in the equations for the flow of a viscous or a plastic substance through a capillary we make the length of the capillary zero, we obtain the identical equation

$$\frac{V}{t} = k\pi R^2 \sqrt{\frac{Pg}{m\rho}} \tag{95}$$

where k is a constant. This is the characteristic and familiar equation for the flow of liquids through an orifice in which the

TABLE LXI.—SIMONIS' EXPERIMENTS ON THE FLOW OF SUSPENSIONS OF ZETTLITZ EARTH THROUGH A 2-MM ORIFICE

Number	Ml NaOH sol.		15	16	17	18	20	22	25	30	35	40	45	50	60	70	80	90	100	110
1	0	Obs.													4.1	8.9	14.8	20	39	58
		Calc.																0	0	0
2	2	Obs.				_f_ = 93.3									9.0	13.3	26.6	45.2	104	234
		Calc.				_f_ = 98.0												0	0	0
3	4	Obs.				_f_ = 84.0									13.8	18	43	180	348	464
		Calc.				_f_ = 83.9											0		221	455
4	5	Obs.				_f_ = 72.2								48		48.5	192	384	588	852
		Calc.				_f_ = 69.8								0			74	308	542	779
5	6	Obs.				_f_ = 60.7						8.5		10.5	200	156	392	666	920	1,176
		Calc.				_f_ = 55.7						0		0	0	173	407	641	875	1,110
6	7	Obs.				_f_ = 42.2				2		120		59	269	414	486	641		
		Calc.				_f_ = 41.6				0		131		0	0	503	737	972		
7	8	Obs.								232	32	450	260	338	660	804	1,068	971		
		Calc.								227	0	461	248	365	599	833	1,067	1,248		
8	9	Obs.				284	50	90		588	360	792	960	746	1,020	1,140		1,301		
		Calc.				276	0	0		557	344	791	908	695	929	1,164				
9	10	Obs.		510	540	612	632		720	900	648	1,044		1,118	1,212				26.9	
		Calc.		543	566	590	637		754	871	674	1,094		1,025	1,259			_f_ = 27.5	
10	11	Obs.	576	528	600	540	624		672	871	996								13.3	
		Calc.	520	543	566	590	637		754	972	988							_f_ = 13.4	
11	12	Obs.		360	480		720			871									0	
		Calc.		543	566		637			871									0	
12	−14	Obs.	372		480		720			972									0	
		Calc.	520		566		637			871									0	
13	18	Obs.			744		720			996									0.0	
		Calc.			566		637			871									0.0	
14	22	Obs.			696		756			996									0.0	
		Calc.			566		637			871									0.0	
15	26	Obs.	636				618			871									0.0	
		Calc.	520				637			996									0.0	
16	30	Obs.					637			871									0.0	
		Calc.																		
H₂O	528	Obs.																		
		Calc.																		

fluidity or mobility does not appear. The table shows that the higher rates of flow may be calculated quite accurately by means of the formula

$$\frac{V}{t} = 23.4(P - f') + 168.7 \tag{96}$$

Historical

A large amount of work has been devoted to the flow of solids. Methods of measuring plasticity, consistency, and hardness have aimed to give a single numerical value to a property which is found to be complex. Plasticity itself has hardly been measured, but rather some property instead which is supposed to be related to it, such as the amount of water required to bring a clay to a given consistency, the tensile strength on drying, the absorptive capacity for certain dyes such as malachite green, the amount of shrinkage on drying, etc. It is no doubt true that these properties are dependent in large measure upon the fineness of grain which also essentially affects the plasticity, but a knowledge of these properties leaves the subject of plastic flow in a nebulous state.

Many investigators have investigated the so-called "viscosity of solids," assuming that solids obey the ordinary laws of viscous flow, and Tammann has identified fluidity with plasticity. Heydweiller (1897) has measured the viscosity of menthol in both the liquid and the solid condition. Weinberg (1913) Dudetzkii (1914) and Pochettino (1914) have measured the viscosity of pitch or asphalt. Segel (1903) worked with sealing-wax and Barus (1893) with marine glue. Barus made the important observation that if the rod of material coming out of the capillary used in his measurements was cut off neatly with a knife, the cylinders thus formed were in a strained condition. They spontaneously change their shape, the advancing end becoming hollowed in and the following end being bulged out. This proof of strain is very similar to that observed by Trouton.

Tresca (1868) did valuable work in forcing metals through orifices and proving that they may be made to flow in a linear manner much as liquids do. It gives good reason for the presumption that it is practicable to measure the friction and mobil-

ity of metals and alloys. The work of Andrade on the different types of flow in metals may be referred to.

Werigen, Lewkojeff, and Tammann (1903) measured the rate of outflow of various metals and arranged the metals in a plasticity series as follows: potassium, sodium, lead, thallium, tin, bismuth, cadmium, zinc, antimony. They observed that with equal pressures and openings, the efflux increases by about 100 per cent for every rise of 10° in temperature. This is shown by the following table:

TABLE LXII.—THE RELATIVE EFFLUX OF METALLIC LEAD THROUGH A SMALL ORIFICE AT VARIOUS TEMPERATURES (AFTER WERIGEN, LEWKOJEFF AND TAMMANN)

Temperature, degrees	Efflux (relative)	Temperature, degrees	Efflux (relative)
0.5	0.8	60.3	42.4
10.4	1.2	70.0	84.3
20.5	2.3	79.3	157.5
30.4	4.7	89.6	211.5
50.7	22.9		

When a wire, which is stretched by a weight, is subjected to torsional vibrations, the amplitudes of the vibrations form a series in geometrical progression, and therefore the logarithmic decrement of the amplitude is a constant. A part of the energy of vibration is given to the surrounding atmosphere and a part is transmitted to the support, but a portion of the energy is dissipated within the wire itself. It is generally agreed that this loss is due to the lack of perfect elasticity in the wire. In other words, the wire when subjected to shearing stress suffers permanent deformation even though the stress is not equal to the elastic limit. This deformation causes a shift in the position of rest, so that as the pendulum passes from its new position of rest to its old position of rest, it does so at the expense of its own momentum and there is thus a loss of energy. This flow is entirely analogous to the flow of various plastic materials such as clay slip and paint, which we have already considered, when the shearing stress is less than the friction.

Since the flow is of the nature of local slippage rather than true plastic flow, strains accumulate and they remain after the stress is removed. The result is the same as that observed by Trouton in pitch, in that the substance tends to creep slowly back toward its old position of rest during a period of time which in pitch is comparatively short but may be observed in metals for hours or even days. The elastic "after effect" has been the subject of exhaustive investigation by Weber (1835), Warburg (1869), Kohlrausch (1863–76), Boltzmann (1876), G. Wiedemann (1879), Pisati (1879), Streintz (1879), Rakkuk (1888), Wiechert (1889) and others.

Kupffer (1860) was inclined to attribute this partial flow of the metal to what he would denominate the fluidity of solids in analogy to the fluidity of liquids. He says, "Il paraît que les molécules des corps solides possèdent la propriété non seulement de s'écarter les unes des autres en produisant une résistance proportionelle aux écarts, mais aussi de glisser les unes sur les autres, sans produire aucune effort. Cette propriété est possédée à un haut degré par les fluides; je le nommerais volontiers la fluidité des corps solides; le coefficient ψ pourrait être appelé coefficient de fluidité; la malléabilité des métaux paraît en dépendre et peut-être aussi leur dureté." According to the present views we would say that this partial flow was evidence of low friction or high mobility.

In harmony with this view, it has been found that the logarithmic decrement of the amplitude of vibration is low in hard metals like steel and high in soft metals like lead. The logarithmic decrement also increases as the temperature is raised but in this respect iron and steel are exceptional below 100°C according to Kupffer, Pisati, and Horton (1905). It will be recalled that sulfur presents a similar exception in the case of liquids.

According to this view, the elastic limit is reached when the shearing stress is equal to the friction constant, for at this value of the stress the material *begins* to yield. But since the deformation takes place with exceeding slowness at this particular stress, a wire may be loaded considerably beyond the elastic limit before the flow becomes appreciable. The yield point naturally depends to some extent upon the rate with which the load is put on.

Just as Trouton found that a given shearing stress produced a

more rapid rate of flow at first than later when the strains were developed to their maximum amount, so it is common experience that metals become harder with working, but that they may be softened again by annealing. In the process of annealing, the plasticity is increased by raising the temperature and thus the strains relieve themselves more quickly than otherwise would be the case.

An entirely different view from that given above has been presented by Lord Kelvin and it has had many followers. Noting that the logarithmic decrement of the vibration is greater in lead and zinc than it is in steel, he reasoned as follows:

"Hence, there is in elastic solids a *molecular friction* which may be properly called viscosity of solids, because as being an internal resistance to change of shape depending on the rapidity of the change, it must be classed with fluid molecular friction, which by general consent is called *viscosity of fluids.*"

However, he further stated:

"But at the same time it ought to be remarked that the word viscosity, as used hitherto by the best writers, when solids or heterogeneous semi-solid-semi-fluid masses are referred to, has not been distinctly applied to molecular friction, especially not to molecular friction of a highly elastic solid within its limits of high elasticity, but has rather been employed to designate a property of slow continual yielding through very great, or altogether unlimited, extent of change of shape, under the action of continued stress."

It has thus come about that the logarithmic decrement has been taken as a measure of the viscosity of a metal, so that according to this nomenclature lead has a higher viscosity than steel and the viscosity of lead increases as the temperature is raised, which point of view is just the opposite of that used by Kupffer and to which we are generally familiar in discussing the viscosity of fluids. Since, however, several investigators have followed Lord Kelvin in his nomenclature, there is danger of considerable confusion. If we hereafter refer to the friction and mobility of solids, the term "viscosity of solids" becomes unnecessary; and we may confidently expect that the friction constant of lead will be found to be lower than that of steel and that it will decrease with the temperature.

In conclusion, we note again, *cf.* page 58, that Reiger (1906) and Glaser (1907) have carefully investigated the question as to whether the laws of Poiseuille may be applied to soft solids, using as their material suspensions of colophony in turpentine. They concluded that with a tube having a radius of 0.49 cm the viscosity was independent of the pressure between the limits of 136 and 2,172 g per square centimeter; and in a similar way it was independent of the length of the tube for lengths varying between 2.4 and 20.6 cm. They found that with a pressure of 1,965 g per square centimeter, if they varied the radius of the tube from 1.52 to 0.34 cm, the viscosity remained constant but for tubes of smaller radii the viscosity rapidly increased until finally the material seemed to have infinite viscosity. This inferior limit is unlike anything observed in the flow of liquids, for the smaller the radius of the tube, the better are the laws of Poiseuille obeyed, and in large tubes the flow is largely independent of the viscosity of the fluid. It seems probable that the use of such very large tubes has prevented Reiger and Glaser from discovering the friction constant just as, in the period before Poiseuille's study of flow in capillaries, the use of large tubes prevented the discovery of the laws of viscous flow. In large tubes the shearing stress is very large in comparison with the friction which may possibly explain the fact that the "viscosity" was found to be independent of the pressure or length of the tube.

We note that the inferior limit of the radius of the tube is increased as the percentage of solid in the mixture is increased. This is what we should expect since this procedure raises the friction constant. With an 80 per cent of colophony the lower limit of the radius was found to be 0.100 cm, with an 85 per cent mixture it was 0.576 cm., and with a 90 per cent mixture it was 1.019 cm. We give below a résumé of the data of Glaser for the 90 per cent suspension of colophony in turpentine, the pressure throughout being 2,040 g. per square centimeter.

The subject of the plasticity of ice takes on exceptional interest and importance in connection with the flow of glaciers and it has been the object of research by many investigators, among whom we mention Pfaff (1875), McConnel (1886), Mügge (1895), Hess (1902), Weinberg (1905) and Deeley and Parr (1914). It is a noteworthy fact that the precipitous moun-

TABLE LXIII.—THE EFFECT OF VARYING THE RADIUS OF THE CAPILLARY
ON THE "VISCOSITY OF A SOLID" (AFTER GLASER)

Temperature, degrees C	Radius, centimeters	Length, centimeters	Time, seconds	Volume, cubic centimeters	"Viscosity," absolute
12.2	1.525	25.1	16,200	0.381	4.59×10^9
12.3	1.241	15.9	43,200	11.20	4.54×10^9
12.3	1.019	15.9	173,000	2.060	4.59×10^9
12.3	0.746	16.0	258,000	0.756	5.62×10^9
12.3	0.576	15.1	171,000	0.129	7.91×10^2
12.3	0.364	15.8	350,000	0.0866	25.2×10^9

tain peaks maintain their sharp outlines through geological ages whereas ice flows steadily in spite of apparent hardness. This indicates that the friction constant of ice is incomparably lower than that of most silicate rocks. Whereas the glacier scrapes its bed to some extent (slipping), there is an abundance of evidence that there is differential flow in the glacier mass, so that although regelation introduces a new factor into the problem, the flow is essentially plastic in its nature.

CHAPTER IX

THE VISCOSITY OF GASES

In 1846, the same year in which Poiseuille published his principal paper on the laws of viscous flow in liquids, Thomas Graham published the first of a series of papers on the "transpiration" of gases through tubes of small diameter, which have great historic interest. Graham sharply differentiated the flow of gases through an aperture (effusion) and flow through a long narrow tube (transpiration); he noted that the resistance of a tube of a given diameter was directly proportional to its length. Also "dense cold air is transpired most rapidly," and his experiments led him to a relation between the time of transpiration and the density of the gas. Graham studied the effect of different pressures and concluded that "for equal volumes of air of different densities, the times of transpiration are inversely as the densities," as exemplified in the following table:

TABLE LXIV.—THE EFFECT OF PRESSURE UPON THE TRANSPIRATION OF AIR (FROM GRAHAM)

Pressure, atmospheres	Observed time of transpiration for equal volumes (relative)	Calculated time
1.0	1.0	1.0
1.25	0.795	0.800
1.5	0.673	0.667
1.75	0.589	0.571
2.0	0.524	0.5

When Clausius proposed the kinetic theory in 1857, all of the properties of gases took on increased interest, and Maxwell in 1861 published a paper in which he discussed the three kinds of diffusion: (1) Diffusion of heat or conductivity, (2) Diffusion of matter, and (3) Diffusion of motion or viscosity. The third or

viscosity is the simplest to obtain and it may be used to calculate the other two, so viscosity played an exceedingly important part in the years that followed in the establishment of the kinetic theory on a firm basis. Maxwell defined the unit of viscosity; and the theory of viscosity and its measurement was rapidly advanced by Maxwell, O. E. Meyer and many others. After many vicissitudes, the conclusion was reached that viscosity is a fundamental property independent of the particular method used in its measurement. Thus, for instance, Millikan (1913) brought together the results for air at 23° by five different methods and found them to agree to within less than 0.1 per cent as given in Table LXV.

TABLE LXV.—THE VISCOSITY OF AIR AT 23°C (FROM MILLIKAN)

0.00018258	Tomlinson	Damping of the swinging of a pendulum	(1886)
0.00018229	Hogg	Damping of an oscillating cylinder	(1905)
0.00018232	Grindley and Gibson	Flow through a large tube	(1908)
0.00018257	Gilchrist	Method of constant deviation	(1913)
0.00018227	Rapp	Transpiration method	(1913)

0.00018240 Average value

Between 12 and 30° the viscosity of air is given by the following formula with an accuracy of nearly 0.1 per cent according to Millikan:

$$\eta_t = 0.00018240 - 0.000000493 \ (23° - t)$$

The reader may, however, be referred to the more recent paper of Vogel (1914).

THE THEORY OF THE VISCOSITY OF GASES

The theory of gaseous viscosity has been so often stated that it need be stated here only in the simplest terms. The viscosity of a gas is given by the tangential force required per unit area to maintain a unit velocity in a plane of indefinite extent at a unit distance from another parallel plane supposed to be at rest, the space between the planes being occupied by the gas. It is assumed that if the shearing force is equal to the viscosity, the velocity v at any point will be numerically equal to its

distance s from the plane which is at rest. If, with Joule, we think of one-third of the molecules as moving in a direction which is at right angles to the shear, then these molecules are the only ones concerned in the transfer of momentum which is the cause of viscosity in gases. Through a unit area of a plane separating any two layers of fluid there will pass per second in either direction $1/6NV$ molecules, N being the number of molecules in a unit volume and V their average velocity as calculated from the kinetic energy. The molecule in passing through the given plane comes from a distance which is equal to the molecular mean free path L, and therefore from a plane in which the velocity is not v but $v - L$ in one direction and $v + L$ in the other direction. The molecule which diffuses into a more slowly moving layer loses momentum represented by $m(v - L)$, and similarly a molecule diffusing into the more rapidly moving layer gains momentum represented by $m(v + L)$, so that the total loss of momentum is

$$\eta = \frac{1}{6}NVm[(v - L) - (v + L)]$$

$$= \frac{1}{3}NVmL$$

or since $Nm = \rho$

$$\eta = \frac{1}{3}\rho VL \tag{97}$$

If the speed of the molecules Ω is the mean value as calculated according to Maxwell's law of distribution, the formula for the viscosity becomes, according to O. E. Meyer (1889),

$$\eta = 0.30967\Omega L \tag{98}$$

Since the length of the mean free path varies inversely as the pressure, whereas the density varies directly as the pressure, it was seen at once that the viscosity of gases should be independent of the pressure. This surprising result was confirmed by O. E. Meyer (1866) calculating out the measurements of Graham, also by the measurements of Maxwell (1866) and O. E. Meyer (1865), and it did much to establish the kinetic theory. With the acceptance of the kinetic theory it can be seen that viscosity measurements give a very convenient and simple method for the determination of the mean free path.

TABLE LXVI.—EVIDENCE FROM MAXWELL (1866) THAT THE VISCOSITY
OF AIR IS INDEPENDENT OF THE PRESSURE

Temperature, degrees Centigrade	Pressure in mercurial inches	Logarithmic decrement of oscillating disks
12.8	0.50	0.15378
12.8	5.52	0.15379
13.3	29.90	0.15398

Warburg and Babo (1882) were the first to prove that the viscosity of a gas fluctuates widely with the pressure in the neighborhood of the critical temperature, using carbon dioxide as their experimental substance. We have already commented upon the data for this substance recently obtained by Phillips.

Kundt and Warburg (1875) measured the viscosity of carbon dioxide by the disk method at pressures as low as 0.1 mm of mercury and they found that the logarithmic decrement of the amplitude of vibrations became noticeably smaller when the pressure became less than about 1.5 mm, the distance between the disks being from 1 to 3 mm. At atmospheric pressure the molecular mean free path of carbon dioxide at 0° is 0.0000065 cm, and at 2 mm the mean free path is therefore approximately 0.02 mm. Since a considerable portion of the molecules depart widely from the mean velocity, we should expect the viscosity to decrease long before the molecular mean free path became equal to the distance between the boundary surfaces. Kundt and Warburg believed that the decrease in viscosity due to the increasing length of the mean free path should not occur so long as the thickness of gas was 14 times the mean free path and they therefore assumed that at high exhaustions there is "slipping" at the boundary. No one has yet explained why a molecule of a rarefied gas is any less likely to give up its translational velocity than a molecule of gas at ordinary pressures. Whether the decrease in the viscosity is due to the increase in the free path or not, the hypothesis of slipping seems improbable, and there may be some other explanation for the results observed. For example, in the case of the experiments of Kundt and Warburg with hydrogen, the decrease in viscosity at moderately low pressures is, according to Crookes, "probably due to the presence of a trace of

foreign gas, most likely water," which seems to have been suspected by Kundt and Warburg themselves.

Crookes (1881) measured the logarithmic decrement of a mica disk swinging in a glass bulb and supported by a glass fiber, using pressures as low as could be measured, by means of a McLeod gage. The gases employed were air, oxygen, nitrogen, carbon dioxide, carbon monoxide, and hydrogen at 15°C. In the case of hydrogen the logarithmic decrement was found to be almost perfectly constant from atmospheric pressure down to 0.25 mm. At about this pressure the viscosity of all gases decreases rather suddenly. With other gases there is a slow decrease with the pressure even from atmospheric pressure, except in a sample of air which contained some water vapor, in which case the logarithmic decrement was at first that of air, but at about 50 mm it decreased rapidly to that of pure hydrogen. In an absolute vacuum we must assume that the fluidity is infinite, hence Maxwell's law must break down at very low pressures.

According to the data of Phillips, Fig. 54, we should expect that Maxwell's law would break down at low temperatures or at very high temperatures. There is a curious dearth of data with which to test out this point. However, a hydrocarbon vapor, "kerosoline," was measured by Crookes and the viscosity was found to decrease rapidly from the highest pressure obtained of 82.5 mm down to 8 mm. Lothar Meyer found in experimenting with benzene that the viscosity of the saturated vapor was smaller the higher the back pressure at the exit end of the capillary tube. At high temperatures we are led to expect that just the opposite conduct will be observed, *viz.*, that the viscosity will decrease as the pressure is *increased*, see Fig. 54, but there is so far as known to the author no data to support this conclusion.

VISCOSITY OF GASES AND TEMPERATURE

From the formula

$$\eta = 1/3\rho VL$$

it is evident that the effect of an increase in temperature will be to increase the mean velocity, but it is not known what effect the temperature may have upon the mean free path, although it

seems most reasonable to assume that the temperature is without effect, in which case we should expect the diffusional viscosity to vary directly as the square root of the absolute temperature.

Maxwell concluded from his experiments that the viscosity varies directly as the first power of the absolute temperature. Barus (1889) worked with air and with hydrogen over a very wide range of temperature from 0 to 1,300° and found that the viscosity increased as the two-thirds power of the absolute temperature. Holman (1877) and (1886)) in a careful investigation of the subject had found the exponent to be 0.77 for air. On the other hand, easily condensible gases and vapors such as mercury, carbon dioxide, ethylene, ethyl chloride and nitrogen peroxide give values of the exponent which are nearly unity, according to Puluj (1876) and Obermayer (1876); but E. Wiedemann (1876) discovered that the value grows smaller as the temperature is elevated, which we might have anticipated since they thus become more nearly like the permanent gases. The viscosity of many vapors increases even more rapidly than the first power of the temperature. Schumann (1884) used the formula

$$\eta = KT^{9\!/\!4}. \tag{99}$$

Sutherland (1893) believes that "the whole of the discrepancy between theory and experiment will disappear if in the theory account is taken of molecular force. * *　Molecular attraction has been proved to exist, and, though negligible at the average distance apart of molecules in a gas, it is not quite negligible when two molecules are passing quite close to one another; it can cause two molecules to collide which in its absence might have passed one another without collision; and the lower the velocities of the molecules, the more effective does molecular force become in bringing about collisions which would be avoided in its absence.

"Molecular force alone without collisions will not carry us far in the explanation of viscosity of gases as known to us in nature, because in all experiments on the viscosity of gases there is a solid body which either communicates to the gas motion parallel to its surface or destroys such motion, so that the molecules of gas must collide with the molecules of the solid; for if the molecules of gas and solid act on one another only as centers of

force, then each molecule of gas when it comes out of the range of the molecular force of the solid must have the same kinetic energy as when it went in, so that without collision between molecules of gas and solid there can be no communication of motion to the gas. If, then, molecules of gas and solid collide, molecules of gas must collide amongst themselves."

In the theory of diffusional viscosity explained earlier it was made plain that there would be viscous resistance even if the molecules failed to collide with each other entirely. But Sutherland's view is in accordance with the one we have developed as "collisional viscosity" in that collisions between the molecules, whatever be the nature and origin of the collisions, have an effect upon the viscosity. Sutherland attributes the effect largely to the attraction between the molecules, whereas the law of Batschinski would lead us to ascribe the effect to the *volume* of the molecules. The two points of view are essentially the same.

Sutherland's theory led him to the formula

$$\eta \propto \frac{T^{\frac{1}{2}}}{1 + \dfrac{C}{T}}$$

or

$$\eta = \eta_0 \frac{1 + \alpha C}{1 + \dfrac{C}{T}} \cdot \left(\frac{T}{273}\right)^{\frac{1}{2}} \tag{100}$$

where α is the coefficient of expansion of a gas and C is a constant. This formula has had the most remarkable success of any that have been proposed, although it does not apply to vapors well. A single example of its performance is given in the following table, using Holman's (1886) data for carbon dioxide at atmospheric pressure.

Examining Sutherland's formula, we observe that when the constant C is small in comparison with the absolute temperature the formula reduces to the simple theoretical formula

$$\eta = KT^{\frac{1}{2}}$$

The discovery, (*cf.* Vogel (1914)), that Sutherland's formula fails at low temperatures indicates that it does not quite correctly take account of the deviation from the simple formula.

Quite in harmony with the above, it is found that the values

TABLE LXVII.—Concordance between Sutherland's Formula and Holman's Data for Carbon Dioxide. $C = 277$, $\eta_o = 0.000,138,0$

Temperature, degrees Centigrade	$\eta \times 10^7$ observed	$\eta \times 10^7$ calculated
18.0	1,474	1,471
41.0	1,581	1,584
59.0	1,674	1,671
79.5	1,773	1,766
100.2	1,864	1,864
119.4	1,953	1,951
142.0	2,048	2,056
158.0	2,121	2,127
181.0	2,234	2,227
224.0	2,411	2,409

of C for different substances increase with the critical temperature or boiling-point of the substance. Rankine (1910) obtained an empirical relation between C and the absolute critical temperature T_{cr}

$$T_{cr} = 1.12C \qquad (101)$$

TABLE LXVIII.—The Relation of the Constant C in Sutherland's Equation to the Boiling-point and Critical Temperature

Substance	T_{cr}, Critical temperature, absolute	C	T_{cr}/C	T_b, Boiling temperature, absolute	C/T_b
Helium....................	9.0	78.2	0.11	4.3	18.3
Hydrogen.................	37.0	83.0	0.45	20.4	4.1
Nitrogen..................	127.0	113.0	1.12	77.5	1.45
Carbon monoxide..........	133.0	100.0	1.33	83.0	1.20
Oxygen....................	154.0	138.0	1.12	90.6	1.52
Nitric oxide...............	179.5	167.0	1.08	120.0	1.39
Ethylene..................	383.6	249.0	1.14	170.0	1.46
Carbon dioxide............	304.0	259.0	1.17	194.0	1.33
Ammonia..................	423.0	352.0	1.20	240.0	1.47
Ethyl ether	467.0	325.0	1.43	307.0	1.06

which suggested to Vogel a similar relation to the absolute boiling temperature T_b

$$C = 1.47 T_b \qquad (102)$$

This formula indicates that C increases considerably more rapidly than the temperature, and since T_b is comparatively large for vapors, the less perfect agreement of Sutherland's formula is partially explained. This, however, is not true of hydrogen and helium which present curious anomalies, as shown in Table LXVIII.

VISCOSITY AND CHEMICAL COMPOSITION

If the mass of a particle in a rarefied gas is increased n-fold by changing its chemical composition, the velocity will be $n^{-\frac{1}{2}}$ times the original velocity, so that the momentum of each

TABLE LXIX.—THE VISCOSITIES OF PERMANENT GASES AND VAPORS AT 0°C

Substance	Molecular weight	$\eta_o \times 10^7$	T_{cr}	$\eta_{cr} \times 10^7$
Hydrogen	2.0	850	31.0	
Helium	4.0	1,871	5.	21
Methane	16.0	1,033	183.	
Neon	20.2	2,981		
Nitrogen	28.0	1,678		
Carbon monoxide	28.0	1,672	133.	
Oxygen	32.0	1,920	154.	
Argon	39.9	2,102	155.6	1,253
Nitrous oxide	44.0	1,362		
Krypton	82.9	2,334	210.5	1,806
Xenon	130.2	2,107	288.	2,266
Ethyl alcohol	46.0	827	513.	
Acetone	58.0	725	510.	
Methyl formate	60.0	838	485.	
Ethyl ether	74.1	689	467.	
Benzene	78.0	689	561.	
Methyl isobutyrate	88.1	701	543.	
Ethyl acetate	88.1	690	523.	
Ethyl propionate	90.1	701	547.	

molecule will be $n^{1/2}$-fold that of the smaller molecule. But the number of excursions of the molecules will be in proportion to $n^{-1/4}$, so that the total loss of momentum will be the same as before, provided only that the number of particles per unit volume remains the same.

In gases at ordinary pressure, there are considerable differences in viscosity ranging from 0.0000689 for benzene vapor to 0.0002981 for neon, but they are inconsiderable as compared with the vast differences we find in the liquid state and these viscosities are measured at 0° and not under corresponding conditions. Table LXIX shows that the vapors have viscosities which are smaller than those of the permanent gases except
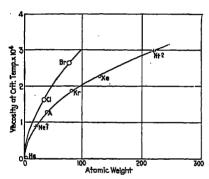
Fig. 82.—The relation between the viscosity of the elements at their critical temperature and their atomic weights.

hydrogen. Their viscosities are so nearly identical that it is not certain whether the viscosity of a given class of chemical compounds such as the ethers differs from that of the esters or ketones. It is quite impracticable with the data at hand to assign any effect to an increase in the molecular weight within a given class of compounds.

Since the viscosities of the permanent gases at 0° are not simply related to each other, it is natural to seek some other basis of comparison, and Rankine (1911) has achieved success along this line by comparing the viscosities of the rare gases η_c and their atomic weights M at the critical temperatures. He finds them related together by the formula

$$\eta_c{}^2 = 3.93 \times 10^{-10} M$$

as depicted in Fig. 82. The critical constants of neon and niton have not yet been determined. Rankine has further found that the same general formula applies to the halogens, but the constant is different being 10.23×10^{-10}. He gives for chlorine $\eta_o = 1,897 \times 10^{-7}$ and for bromine $\eta_c = 2,874 \times 10^{-7}$ (*cf.* Fig. 82). Were we to use the molecular weights instead of the atomic weights, the constant would be 5.12×10^{-10} which is nearer that of the rare gases but still not identical with it.

The Viscosity of Gaseous Mixtures

Since in a rarefied gas the viscosity is proportional to the number of molecules in a unit volume, *i.e.*, to the pressure, the viscosities will be additive when gases are mixed in varying percentages by volume; but since the viscosity of a rarefied gas is also independent of the weight of the molecules, the law loses its significance.

In gaseous mixtures at ordinary pressures the simple deduced formula

$$\eta = \frac{1}{3} \rho VL$$

still applies, it being merely necessary to find the appropriate mean values of ρ, V, and L. This has been done by Maxwell (1868) and Puluj (1879), and one obtains the formula (*cf.* Meyer's *Kinetic Theory of Gases*, page 201 *et seq.*)

$$\eta = \eta_1 \frac{\left(\dfrac{p_1}{p} + \dfrac{p_2 m_2}{p \, m_1}\right)^{\frac{1}{2}}}{\left\{\dfrac{p_1}{p} + \dfrac{p_2}{p}\left(\dfrac{\eta_1}{\eta_2}\right)^{\frac{1}{2}}\left(\dfrac{m_1}{m_2}\right)^{\frac{3}{4}}\right\}^{\frac{1}{2}}} \tag{103}$$

Graham (1846) observed that mixtures of oxygen and nitrogen or oxygen and carbon dioxide in all proportions have rates of transpiration which are the arithmetical mean of the two components. Thus for air,

$$0.0001678 \times 0.7919 = 0.0001329$$
$$0.0001920 \times 0.2081 = 0.0000399$$

Calculated viscosity of air...........	0.0001728
Observed viscosity of air...........	0.0001724 Vogel (1914).

Graham and others have noticed that when hydrogen is mixed in

small amounts with other gases, as carbon dioxide or methane, the viscosity of the mixture is much greater than would be calculated by the simple formula of additive viscosities. In these cases Puluj (1879) and Breitenbach (1899) have found that the more complicated formula (103) gives good agreement.

Viscosity of Gases and Diffusion and Heat Conductivity

We note that the diffusion coefficient D in a mixture of gases is

$$D = \frac{1}{8}\pi(N_2 L_1 \Omega_1 + N_1 L_2 \Omega_2)/N \tag{104}$$

N_1, L_1, and Ω_1 being the number of molecules of the first kind of gas per unit volume, the length of the mean free path, and the mean speed respectively, etc. Also $N = N_1 + N_2$. Since the length of the mean free path can most easily be calculated from the viscosity, it becomes possible to calculate the diffusion coefficient from the viscosity.

In the conduction of heat the two kinds of gas become identical, hence the above equation becomes

$$D = \frac{1}{8}\pi\Omega L \tag{105}$$

If we neglect the small difference between Ω_1 and Ω due to temperature difference the conductivity of heat k becomes

$$k = \frac{1}{8}\pi\Omega L\rho C_v \tag{106}$$

C_v being the specific heat of the gas at constant volume, and combining this equation with the viscosity Eq. (97) we obtain

$$k = C\eta C_v \tag{107}$$

C being a constant (*cf.* Eucken (1913)).

Determination of the Ultimate Electrical Charge

It is well known that Sir J. J. Thomson (1898) devised a method for measuring the charge on the particle of a rarefied gas e by observing the rate of fall under gravity of the particles of an ionized fog which had been produced by sudden expansion and then observing the rate of fall of a similar cloud when it is subjected to the action of a vertical electrical field of known intensity superimposed upon gravity.

If v is the velocity of a droplet of mass m, density ρ under the action of gravity alone, and v_1 its velocity when under the influence of the electrical field whose strength is X in electrostatic units, then

$$\frac{v}{v_1} = \frac{mg}{mg + Xe} \tag{108}$$

Applying Stokes' Law, Eq. (62), to the sphere whose volume is $4\pi r^3/3$, we obtain

$$e = \frac{4}{3} \frac{\pi g}{X} \left(\frac{9\eta}{2g}\right)^{3/2} \frac{(v_1 - v)}{\rho^{1/2}} v^{1/2} \tag{109}$$

A beautiful application of this method has been made by Millikan (1909, etc.). He has found the most probable value for e to be 4.69×10^{-10}. This leads to the number of molecules in a gram molecule $N = 6.18 \times 10^{23}$ and the mass of the hydrogen atom as 1.62×10^{-24} g.

Chapman (1916) and Rankine (1920–1) have calculated the diameters of the atoms of the monatomic gases from determinations of the viscosity. They regard the atoms as hard spheres having the well-defined absolute diameters given below.

ATOMIC DIAMETERS OF SOME OF THE NOBLE GASES AFTER RANKINE

Gas	Viscosity	Crystal measurement
Neon	2.35×10^{-1}	61.30×10^{-1}
Argon	2.87×10^{-1}	2.05×10^{-1}
Krypton	3.19×10^{-1}	2.35×10^{-1}
Xenon	3.51×10^{-1}	62.70×10^{-1}

These values agree very well with those obtained from van der Waal's equation but they are somewhat greater than the diameters of the outer electron shells of the atoms as obtained by Bragg from his crystal measurements.

SUPERFICIAL FLUIDITY

The viscosity of a liquid may change, and it may change in a quite extraordinary manner, as the boundary of the liquid is approached. This must of necessity result wherever the surface tension is such as to bring about a change in concentration at the boundary. We should therefore naturally expect soap and saponin solutions to show this phenomenon. Experimentally this field of study has not been much explored although, as we shall attempt to show, the promise of reward is very great and the need of such study in industry is pressing. However, Stables and Wilson (1883) have proved that a saponin solution has a viscosity at the surface which is 4,951 as compared with 3.927 for the surface of pure water. The viscosity was measured by the oscillations of a circular nickel-plated brass disk, of 7.625 cm diameter and 0.2 cm thickness, which was suspended in the liquid by means of a wire 119.8 cm long. As soon as the solution was allowed to rise 0.15 cm above the disk the viscosity fell to its normal value.

The viscosity found by Stables and Wilson indicates that the surface layer of a supposedly dilute solution may nevertheless have a viscosity which is over a thousand-fold that of water at 20°C (1,260 cp) or about the viscosity of castor oil. But for very small stresses, the viscosity may be still higher, for it is to be particularly noted that in a saponin solution a pendulum does not oscillate isochronously. Thus in one experiment with vibrations of large amplitude, Stables and Wilson found the time of vibration to be 10.52 seconds, whereas with small amplitudes the time of vibration was 9.73 sec. This would indicate that with very small stresses the viscosity might be found to be infinite, which would mean that we are here again dealing with plastic flow.

The experiments of Stables and Wilson need confirmation and

extension with our more recent knowledge of the nature of flow in mind, but whatever the surface of a given saponin solution may be, we may profitably distinguish three typical cases: (*A*) where the superficial layer is a true solution but of different concentration from the interior and is in contact with it own vapor or some gas; (*B*) where the surface is made up of a layer of immiscible liquid, which may be so thin as to be imperceptible by ordinary means; (*C*) where the surface is formed either by a continuous solid or by solid particles in more or less intimate contact with each other. It is evident that in the last two cases we are dealing not with the superficial fluidity of the liquid but of a heterogeneous mixture of liquid-liquid or solid-liquid respectively.

Soap solutions perhaps afford the best examples of the first case and if such solutions have extraordinarily high superficial viscosity, it serves to explain the stability of the soap bubble. The liquid between the two highly viscous surfaces can proceed downward very slowly in so narrow a space.

Oil films on water give frequent examples of the second sort, and the use of oil "to calm troubled waters" is a practical application of superficial viscosity in the damping of vibrations. The simple harmonic motion of the wave causes the particles to move in vertical circles, so that an oil film is alternately stretched and compressed. The water underneath not being subjected to this same tendency is pulled along by the oil film and in this viscous flow energy is of course dissipated. A method for the measurement of viscosity by Watson (1902) depends upon the damping of small waves in a free surface, and apparently this method is capable of being used to measure superficial viscosity, but this appears not to have been attempted.

The connection of superficial fluidity with emulsions must be mentioned at this point although we cannot stop to discuss it. We can merely refer the reader to the fascinating studies of Plateau, Quincke, and Lord Rayleigh upon the nature of contaminating films. The recent paper by Irving Langmuir (1919) on the theory of flotation is very suggestive.

Many of the examples which we would naturally cite as examples of the second case given above may really be examples of the third instead. It is certain that in most emulsions a third substance is necessary to stabilize it and it may give rigidity. Scums

are apparently examples of this class.   Gurney (1908) in investigating the contamination of pure water surfaces on standing, says "Water surfaces become noticeably rigid in a few hours or days: depending on the previous history of the fluid.   Vigorous stirring destroyed the rigidity of the surface."

To prevent possible misunderstanding, it must be stated again that rigidity in foams and emulsions arises largely from the fact that during shear the bubbles of a foam or the globules of an emulsion are distorted and may be disrupted, and thus work is done against the forces of cohesion opposing such disruption.

Superficial viscosity has heretofore been considered at a free surface only.   Such a view is too narrow as it would leave the most important examples out of consideration and from the theoretical aspect the extension of our conception of superficial fluidity involves no difficulty whatever.   Having made this extension, the phenomenon of slipping falls into the third case, but the fluidity near the boundary is *higher* than that of the main body of material.   Henry Green (1920) has studied this slippage under the microscope, using for observation paint colored with a little ultramarine, which may be subjected to shearing stresses in a capillary tube.   With small stresses the shear takes place exclusively in the region near the boundary, but when the stress becomes greater than the yield value of the paint, the shearing takes place throughout the material.   Green reasons that it is this mixture of the kinds of flow which causes the shear to fail to be a linear function of the shearing stress, particularly when those stresses are near the yield shearing stress.   In the above example, the layer next to the boundary was more fluid than the main body of material, but more often the opposite is the case, the fluid near the boundary is less fluid, and we might therefore consider the general subject of adsorption under this head.   And we would then show that it is possible to make a fractional separation of fluids by simply passing them through capillary tubes.   Such a separation of a mixture into its components by means of capillary flow has actually been demonstrated, as in the case of petroleum forced through clay by Gilpin and his co-workers (1908).[1]   Since the surface area of a capillary varies as the first power of the

[1] *Am. Chem. J.* **40**, 495 (1908); **44**, 251 (1910); **50**, 59 (1913).

radius whereas the volume of flow varies as the square of the radius, Eq. (6), we may expect to find the effects of superficial fluidity shown to the best advantage in very fine tubes.

There are a variety of causes which may cause the fluid near the boundary to have a different fluidity. The most important cause results from the selective adhesion of the components of the fluid for the solid. If one of the components of the fluid is more strongly attracted than another, separation becomes possible, and the magnitude of the fluidity of the mixture as measured will theoretically be affected The adhesion between solid and liquid or liquid and liquid is doubtless just as specific a property as is the better known cohesion or surface tension of liquids and we are coming to understand the nature of adhesion better through the efforts of Langmuir (1919) and Harkins (1920). We have seen that it is possible to greatly affect both the friction and the mobility of plastic substances by the addition of small amounts of acid or alkali. Just what happens in such cases might be subject to dispute, but it is certain that small amounts of substances adsorbed on to the surface of a solid may entirely change the character of the solid which is in contact with the liquid. Thus Henry Green (1920) has observed that the addition of small amounts of gum arabic to a suspension may greatly decrease the yield value and increase the mobility, in spite of the high viscosity of gum arabic solutions. This is interpreted as being due to the decrease in adhesion between the suspended particles. The well-known work of Schroeder (1903) upon the effects of electrolytes on the viscosity of gelatine and of Handowsky (1910) upon serum albumin should also be referred to.

We have already proved on page 86 that if any cause results in the fluid near the boundary becoming different from the remainder of the liquid, the resulting fluidity will be changed. This theorem is therefore useful in explaining superficial fluidity. We will now prove that the components of a mixture under these conditions will undergo partial separation. The conditions will be made more general by using the non-homogeneous mixture considered on page 86. Considering the mixture as made up of the two components A and B, arranged in alternate plane layers, the total quantity of A flowing in a unit of time, regardless

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of whether it is derived from the fluidity of A or B, is obtained from the terms of Eq. (26) containing r_1, and is

$$U_1 = \frac{R^2P}{2}\Big(a^2\varphi_1 + \frac{n-1}{n}ab\varphi_2\Big)$$

and similarly the rate of flow of component B is

$$U_2 = \frac{R^2P}{2}\Big(b^2\varphi_2 + \frac{n+1}{n}ab\varphi_1\Big)\cdot$$

There will be separation of the two components only when the thickness of the different layers is considerable or when the passage through which the substances are forced is very small, for in either case n will be small. If $n = \infty$,

$$\frac{U_1}{U_2} = \frac{a}{b}$$

and there will be no separation at all. The separation may be calculated from the expression

$$\frac{U_1}{U_2} = \frac{a}{b}\cdot\frac{na\varphi_1 + (n-1)b\varphi_2}{(n+1)a\varphi_1 + nb\varphi_2} \tag{110}$$

When $n = 1$, the component A will flow at only one-third of the rate of B, even though the two components have the same fluidity and are present in equal proportion; and even if the fluidity of B is zero, it will flow twice as rapidly as A, under the above conditions. It follows that the flow of B is greatly increased by making the fluidity of A large, this being the layer in contact with the stationary boundary.

An ingenious application of the principle of superficial fluidity was made by the Southern Pacific Railroad,[1] when it was found that the pressure required to pump certain heavy oils through long pipe lines was inconveniently large. The problem was to get the maximum flow of oil for a given expenditure of energy and with a given diameter of pipe. By using a *rifled* pipe and injecting about 10 per cent of water along with the oil, the water was thrown to the outside of the pipe by the centrifrugal action caused by the rifling, producing a high superficial fluidity; and thus, by a seeming paradox, the water lubricated the oil so that the delivery became from 8 to 10 times what it would have been had the water not been added.

One may demonstrate the effect of superficial fluidity very

[1] *Engineering Record*, **57**, 676 (1908).

simply by comparing the times required by gravity to empty two pipettes filled with a heavy oil, each of the pipettes being similar in every respect except that one is moistened with water previous to filling with oil.

In an experiment by the author at 25°C and a pressure of 60 g per square centimeter a given volume of water required 33 sec. and the same volume of cottonseed oil required 1,640 sec. A mixture was then used containing one-third oil and two-thirds water by volume. Had the heavier water flowed completely through the capillary ahead of the oil, the time of flow should evidently have been $22 + 547 = 569$ sec.; yet only 391 sec. were actually required which is less than the time theoretically required by the oil alone. The difference of 178 sec. is due to the water forming a lubricating film for the oil as the water drained out through the capillary.

Rate of Absorption.—It is appropriate here to show how the rate of absorption of a fluid into a porous material depends upon the fluidity of the medium. From Poiseuille's Law, Eq. (8), it follows that the rate $\dfrac{dl}{dt}$ at which a liquid enters a long capillary tube under the driving force P will be

$$\frac{dl}{dt} = \frac{Pr^2\varphi}{8l}.$$

If the capillary is very small, the surface tension γ exerts a force $\dfrac{2\gamma}{r}$ which must be added to the external pressure and this force arising from the surface tension may be so great that the external pressure is negligible in comparison, in which case

$$\frac{dl}{dt} = \frac{\varphi\gamma r}{4l}$$

and by integration

$$l^2 = \frac{\varphi\gamma}{2} \cdot rt$$

The quantity of $0.5\varphi\gamma$ is called the *coefficient of penetrance* of the fluid and it is a measure of the tendency of a liquid to penetrate a given material which it wets. (*Cf.* Washburn *Physical Chemistry*, 2d ed., p. 62.)

The distance that a liquid will penetrate a given porous material due to capillary action alone is often of practical importance.

From the above equation we see that this distance is proportional to the square root of the fluidity, the surface tension, the radius of the capillary and the time.

It is generally assumed that the material of the pore walls is immaterial so long as the walls are wet by the liquid.   Adhesion between solid and liquid may come into play in certain cases making such an assumption fallacious, as already pointed out. Experiments on the impregnation of fabrics, belting, wood *et cet.* with oils, gums, paints *et cet.* have shown that thorough drying of the former materials has an extraordinary effect upon the penetration of the latter.   This may be due to increasing adhesion although it may be explained in some other way.

CHAPTER XI

LUBRICATION

When a solid substance is subjected to a shearing stress, it undergoes plastic flow if the stress is greater than the yield value of the material. In this process of shear, lateral stresses arise and if the material is not supported laterally by sufficient pressure, rupture of the material will finally result. These surfaces formed by rupture slide over each other according to the laws of solid friction stated by Coulomb. The surfaces are separated for the most part by a layer of fluid which may be air, water, oil, a layer of oxide, etc. So two surfaces formed by a rupture as, for example, two broken pieces of porcelain do not adhere together firmly even when they seem to fit together very nicely. So also the resistance to movement between ordinary smooth surfaces is far less than the resistance to plastic flow.

If, however, sufficient force is brought to bear between two sliding surfaces of similar material, there will occur, far below the melting point of the substance, a welding together of the surfaces into a more or less compact whole, unless there is present some substance which prevents such welding. Two surfaces of glass ordinarily touch each other at very few points and they do not adhere strongly, but when the two surfaces are ground to an optical surface and cleaned, it is difficult to separate the two surfaces without tearing them, after they have been brought together. A motor bearing which has been carefully fitted by "lapping in" may be ruined completely by a slight turn with the hand after the surfaces have been cleaned and again brought together. Powdered metals adhere strongly when subjected to heavy pressures, even at temperatures considerably below the melting point. The Johannsen blocks used in gage testing are made of hardened steel with surfaces which are exceptionally true. When these blocks are placed one on top of the other, the adhesion between them is so great that a pile of

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them several inches high can be raised by lifting the topmost one.   In imperfect lubrication we first have excessive wear, then scoring of the bearings and finally seizure with a more or less complete welding together of the surfaces.   Thus there is a considerable mass of evidence to prove that whenever two clean surfaces come together they adhere and thus the conditions for plastic flow may be reestablished.   The problem of lubrication is therefore to substitute as far as possible fluid friction for the enormously higher resistance to shear in plastic flow.

According to the above view, "solid friction," as ordinarily observed, is intermediate between true plastic flow and true viscous flow.   Under favorable conditions it approaches closely to simple viscous flow, whereas under very unfavorable conditions it may approach the conditions for plastic flow.   It is clear therefore that the coefficient of solid friction may vary within the widest limits depending upon the condition of the bearing surfaces, the temperature, speed, and character of the lubricant.

Thus at the outset we may state that it is impossible to specify the lubricant that will be most suitable for a given machine, provided that that machine works at variable speeds, temperatures and loads, and where the bearings are continually subject to wear due to defective lubrication.   On the other hand, if bearings are perfectly lubricated and run under constant conditions, there is practically no wear, so that the problem to find the most suitable lubricant has a definite solution.   With the steady advance of industrial development, the theory of lubrication takes on increasing interest.

The laws of solid friction may be stated as follows: (1) When two unlubricated smooth surfaces slide over each other, the frictional resistance P varies directly as the load W or

$$P = \zeta\,W \tag{111}$$

and the coefficient of friction ζ is defined as the ratio between the friction and the load.

2. The force P_0 required to maintain an indefinitely small rate of shear, the so-called *static friction*, is greater than when the rate of shear is appreciable.   The dynamic friction is independent of the velocity.

3. The friction is independent of the area of the surfaces in

apparent contact, within wide limits. The surfaces must, however, be large enough so that the surfaces remain intact.

Since it is impracticable to obtain a pair of smooth and entirely unlubricated surfaces, it is needless to say that these laws are very inexact. As already intimated, well-fitting and clean surfaces of similar material would probably seize and follow the laws of plastic flow, which are very different from the laws given above. They have, however, both historic interest and practical usefulness.

Just as the laws of solid friction are superficially unrelated to the laws of plastic flow, so these laws are also in sharp contrast to the laws of viscous flow which apply to well-lubricated surfaces. With well-lubricated surfaces we have the relation

$$P = S\eta \frac{dv}{dr}$$

where S is the area of surface in contact, dv is the velocity and dr is the thickness of the oil film. According to this relation:

1. The frictional resistance P is independent of the load.

2. The friction is directly proportional to the velocity and is therefore zero when the velocity is zero.

3. The friction is also directly proportional to the area of surfaces in contact.

In view of the absolute antithesis between these two sets of laws, it is not surprising that the results of the study of friction as recorded in the literature are often contradictory. We may, however, state broadly that slow-moving, poorly lubricated surfaces follow approximately the laws of solid friction, whereas rapid-moving and hence necessarily well-lubricated machinery, such as electric dynamos and motors, follows the laws of fluid friction. Most bearings are imperfectly lubricated and follow neither set of laws exactly.

Petroff (1887) seems first to have applied the laws of fluid friction to lubricated bearings testing out his views by experiment.

Most important in its relation to the development of the theory of lubrication is the experimental work of Beauchamp Tower (1883–4), undertaken at the instance of the Institution of Mechanical Engineers. His experiments were conducted with extreme care and under varied and well-chosen circumstances. His results, as obtained under *ordinary* conditions of lubri-

cation, "so far agree with the results of previous investigators as to show the want of any regularity." He perceived that this difficulty was due to irregularity in the supply of lubricant, so he conducted experiments in an oil bath. Not only was he thus able to obtain a high degree of regularity but he proved that the journal and bearing are completely and continuously separated by a film of oil. This film is maintained by the motion of the journal against a hydrostatic pressure in the oil, which at the crown of the bearing was shown by actual measurement to be 625 lb. per square inch greater than the pressure in the oil bath.

Tower demonstrated that even with an oily pad in contact with the journal, the results were regular although the results were different from those with the oil bath. Of lubrication less than that afforded by the oil pad he says: "The results, generally speaking, were so uncertain and irregular that they may be summed up in a few words. The friction depends on the quantity and uniform distribution of the oil, and may be anything between the oil bath results and seizing, according to the perfection or imperfection of the lubrication."

These experiments of Tower are indeed a landmark in the development of the theory of lubrication for they stimulated various investigators such as Osborne Reynolds, Stokes, and Lord Rayleigh to apply the fundamental hydrodynamical equations to the results obtained. And the labors of Reynolds, continued by Sommerfeld (1904) and Michell (1905), have in fact enabled us to reach a complete solution of the problem of lubrication in certain very special cases. The mathematical integrations have generally proved very difficult.

REYNOLDS' THEORY OF LUBRICATION

The model of viscous flow which we have considered, page 5, does not give rise to any pressure at right angles to the direction of flow, hence it is unable to sustain a load permanently and will not serve for practical lubrication.

Case I. Parallel Surfaces Approaching with Tangential Motion. Let AB in Fig. 83 represent the section of a surface which is moving with the uniform velocity U in respect to the bearing block CD, each being of indefinite length in the direction perpen-

dicular to the paper. As soon as a load is placed on the bearing block, the liquid begins to be squeezed out from between the surfaces. If this space is divided originally into the equal areas indicated by the dotted lines, these lines, moving with the fluid, will after a time occupy the positions of the curved lines; and the distances moved by the particles are shown by the distances between the corresponding points on the two sets of curves, as *QP* for the point *P*, and the slopes of the curves indicate the directions of the forces in the fluid just as if the lines were stretched
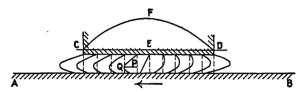
Fɪɢ. 83.—The simplest case of lubrication. Two parallel, plane surfaces.

elastic threads. The pressures exerted upon different points along *CD* are shown in the curve of pressures *CFD*, the pressures being proportional to the vertical height above the line *CED*. At the center of the block the pressure is a maximum and the liquid is squeezed out to the right and left of this section. For this section alone, there is a uniform variation of velocity from *AB* to *CD*, such as would be true of all sections, if the surfaces *AB* and *CD* were not approaching.

Case II. Surfaces Inclined—Tangential Movement Only.— If now the bearing block is tilted, we have fulfilled the necessary condition for continuous lubrication, for the bearing is able to sustain a load without the surfaces approaching each other.

Were we to assume that in this case the velocity varies uniformly from *U* at *AB* to zero at *CD*, the quantity of fluid passing any cross-section *MN* would be proportional to *MN* × *U*/2, or simply to *MN*. But since the quantity of fluid passing every cross-section must be the same, there must be an outflow to the right and left of the cross-section *M'N'*, at which the pressure is a maximum, so the flow at any section *MN* is

$$(MN - M'N')U/2 \qquad \qquad \bullet$$

At the cross-section *MN*, the velocity varies uniformly from

AB to *CD*, but the point of maximum pressure *M* is not at the center of the block nor is it necessarily the point of application of the resultant pressure exerted on the block.

If the bearing is free to move, it will move either up or down until the pressure is just equal to the load. As the load is increased, the surfaces approach each other, which increases the friction and thereby the pressure so that equilibrium is restored. But the point of application of the resultant pressure changes with the load provided that the inclination of *CD* remains the same.

Case III. Revolving Cylindrical Surface—Bearing Surface Flat.—The curves of motion are represented in Fig. 84. To the
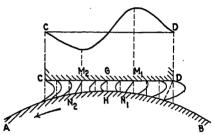
FIG. 84.—Simple continuous lubrication.

right of *GH* which is the point of nearest approach of the surfaces, the curves are similar to those in Case II. At the left of *GH*, the curves are quite the reverse of those on the right, being convex toward a section M_2N_2 on either side, just as they are concave to a section M_1N_1 on the right. The reason for this is that with a uniformly varying velocity more fluid would be brought in at the right of M_1N_1 than would pass the section *GH*, hence the fluid must flow outward from M_1N_1, where the pressure is a maximum in both directions. So at the left of *GH* more fluid would be carried away than arrives through *GH*, hence an inflow is necessary to the right and left of the section of *minimum* pressure M_2N_2. The fluid pressure acts to separate the surfaces at the right and to draw them together at the left hence there is a couple of forces resulting.

If the bearing is cut away at the left of *GH*, the negative pressures may be eliminated.

If the oil supply is limited, the oil may not wet the entire bearing but form an oil pad in the region of *GH*, the pressures of course reaching a zero value at the points where the oil surface meets the bearing surface.   If *d* is the thickness of the oil film outside of the pad, the quantity brought up to the pad per second will be *Ud*, and the quantity which passes the section M_1N_1 where the velocity varies uniformly is $M_1N_1U/2$, and since there is no accumulation of oil, these two values must be equal and

$$M_1N_1 = 2d$$

also

$$M_2N_2 = 2d$$

Case IV.   Revolving Cylindrical Surface—Bearing also Cylindrical.—In a very common example of lubrication we have a cylindrical journal partly or wholly surrounded with the bearing or "brass" *CD* in Fig. 85.   The oil is drawn up into the space *BD*
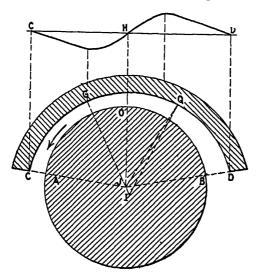
Fig. 85.—The lubricated journal and bearing.

and creates a pressure which is a maximum at *Q*.   The point of nearest approach between journal and bearing is not at the middle of the bearing *O* but at a point some 40° further on at *G* toward the so-called "off-side" of the bearing.   This is the opposite to what happens in the unlubricated bearing, for

the point of nearest approach is then on the "on-side." Only when the bearing is unloaded does the point of nearest approach coincide with the middle of the brass, O. As the load increases the point G moves from O up to a certain maximum value after which it recedes toward O, resulting finally in a discontinuity in the oil just as in the case of a limited supply of oil.

We have considered only bearings of unlimited length, whereas in practical bearings the lubricant is squeezed out at the sides, as well as at the ends. Michell (1905) has made a study of the changes of pressure in the oil film of bearings of various shapes. Generally speaking the integrations necessary to define the exact relations between load, speed and the friction have not been effected.

The theory of lubrication is not inconsistent with the experience that the friction in limited lubrication is proportional to the load and independent of the velocity. Increase of load will result in a diminution of the distance between the bearing surfaces, a lengthening of the oil-pad, and therefore an increase in the resistance. Increasing the velocity increases also the resistance, but it also increases the pressure and therefore the distance between the surfaces, provided that the load is kept constant, and this produces a decrease in the resistance.

For further details of the development of this very important subject the reader is referred to the original papers of Petroff, Tower, Reynolds, Sommerfeld, Michell, Lasche to name but a few.

LUBRICATION AND ADHESION

In the early use of lubrication, fixed oils and greases were depended upon almost exclusively. The fixed oils, that is the non-volatile oils of animal or vegetable origin, are expensive, they may become gummy and rancid, which interferes with proper lubrication and the acids developed may corrode the machines. These oils moreover often partially solidify when only slightly cooled. The range of viscosities obtainable is also restricted by the small number of oils available in any quantity. With the advent of mineral oils, these troubles were all overcome, so the battle which was waged between the mineral and the fixed or fatty oils was short and apparently decisive. The

purveyors of the fatty oils claimed that their oils possessed greater "oiliness," "body" or "lubricating value," but since these claimants seem never to have proved their case by the actual measurement of "oiliness" and since modern industrialism requires vastly more oil for lubrication than could possibly be met by the available supplies of fatty oils, the conception of the property of oiliness has gradually become a sort of will o' the wisp vaguely referred to in treatises on lubrication, and effectively used by energetic salesmen in convincing a prospective buyer of the superiority of a given brand of oil over all others. The theory predicted that so long as the viscosity was sufficient to produce the necessary pressure required to carry the load, it was of no moment what the chemical nature of the lubricant might be, provided only that the quantity of lubricant was ample. The practice has therefore been to use an oil which is much more viscous than is really necessary and to accept a loss in power in order to insure against any discontinuity in the oil film.

There are, to be sure, many instances which might be cited where an experienced engineer has cooled a hot bearing by substituting a fixed oil with which he was familiar for the mineral oil in use. However, in comparing two oils used for practical lubrication, there are so many factors which may affect the comparison such as the quantity of oil, the speed, load, temperature of the oil film, the condition of the bearing surfaces, that instances which might be cited are easily discredited by the skeptical. Nevertheless, there is a growing demand for lubricants which will be less wasteful of power and which will at the same time give the maximum assurance that the bearings will not be injured in use. With the aeroplane in particular, it is necessary to keep the motor going at all hazards during most of the period of flight, and an overheated bearing may easily cause the complete wreckage of the machine in mid-air, so the selection of the best lubricant for severe conditions and the question of "oiliness" becomes now vitally important. Perhaps the clearest evidence on this point is obtained from cutting lubricants.

Cutting Lubricants.—It is the well-nigh universal testimony of mechanicians that in certain cutting operations, fixed oils are absolutely necessary and that mineral oils will not serve as a satisfactory substitute. Voluminous correspondence with large

shops all over this country, with concurring evidence from Great Britain, establishes the fact that fixed oils, preferably lard oil, are superior to all others. This is particularly true in operations such as "parting off" soft steel, in threading wrought iron or steel, in drilling deep holes in steel as in the manufacture of gun barrels. The tool keeps its edge longer, the machine runs more smoothly, there is less heating, a much greater speed may be attained, the chip is less serrated and therefore longer, the cut surface is smoother and much closer dimensions may be obtained, when using lard oil or its equivalent.

On the other hand, there are certain operations such as planing and reaming where a lubricant is not required. In others such as sawing metals a liquid may be used merely to cool the work.

No lubricant is ordinarily used in cutting cast iron, brass or aluminum. Wrought iron and "draggy" metals require a lubricant.

Between the two extremes of those operations and materials which absolutely require a fixed oil and those which require no liquid at all, there are a great number of classes of work in which mineral oils are satisfactory but where aqueous soap solutions or oil-emulsions are widely used and found to be highly satisfactory. In these cases the oil or water serves to reduce the heating of the work and the tool, and the soap or soda prevents the rusting of the machine. Fixed oils are often a needless extravagance or positively disadvantageous.

Where lard oil is required it is not primarily to conduct away the heat, for the operation may be a light surfacing operation where the heat developed is slight as in the cutting of fine micrometer screws. Its superiority does not depend on its peculiar viscosity because a mineral oil possessing the same viscosity in no way shares its superiority.

It is true that mineral oils increase in fluidity, when heated, more rapidly than fatty oils, but castor oil is exceptional in this respect resembling the mineral oils and yet it appears to be a very useful cutting oil and lubricant.

It has also been suggested that pressure might decrease the fluidity of the mineral oils less rapidly than that of the fixed oils, but this explanation appears to be not even qualitatively correct (*cf.* page 89, Report of the Lubricants and Lubrication Inquiry

Committee. Department of Science and Industrial Research. (London)).

The surface tensions of mineral and of fixed oils are not materially different. These oils are however very different in one important respect *viz.*, that the fixed oils all have an active chemical group which gives them a strong adhesion for metals, so that such an oil is not readily squeezed out from between two metallic surfaces (*cf.* Langmuir (1919), Harkins (1920), and Bingham (1921)). Lord Rayleigh (1918) has shown that a layer of lubricant of
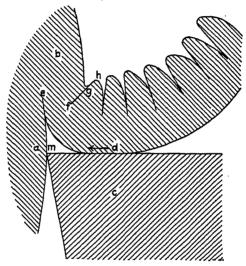
FIG. 86.—Illustration of the necessity for high adhesion in an oil which is to have the best lubricating quality.

monomolecular thickness possesses truly remarkable properties in reducing the friction between solid bodies of similar material, the contamination probably serving to prevent the welding together of the surfaces. According to Langmuir (1920) such a film formed from paraffin oil can be readily removed by a gentle stream of running water from platinum, glass, etc., but a film formed by oleic acid cannot be thus removed.

To get a clearer idea of the action of a cutting lubricant we will follow the operation of an Armstrong parting tool in cutting off disks from a rod of soft steel 1¾ in. in diameter, using a lathe with a constant speed and feed and as lubricants a definite amount of lard oil or of mineral oil of the same viscosity. Some 30 disks were made with lard oil and at the end there was no evidence

that the operation was not as satisfactory as at the beginning. The disk shown in the left of Fig. 86 was perfectly smooth, and there was little evidence of heating and on inspection the tool was found to be not even slightly dulled. The chips shown below the disk were only slightly serrated.

On substituting the mineral oil heating began at once, the surface of the disk shown at the right of the figure was very rough, the chips were deeply serrated, and the tool so dulled that it failed completely on cutting the fourth disk. On examining the cut in the bar at the time of failure, shown in the middle of the

FIG. 87.—Illustration of the forming of a chip in the cutting of metals and of the function of the lubricant.

figure, one can plainly see two beads of metal flowing ahead of the tool and gouging into the bottom of the cut. A burr is being thrown up at the left.

The operation of a tool in cutting is illustrated diagrammatically in Fig. 87. The metal *b* is being cut away by the tool *c*, a chip *f* being formed which bears down heavily upon the tool at a point *d* some distance back from the point. That this is the actual case is proved by many facts. For example, a tool in use is often gouged out by the shaving at some distance back from the point, and there is sometimes found a "bead" of metal

welded to the tool at this point. The tool therefore pries the chip away rather than cuts it, and the point of the tool merely clears up the surface, so long as the tool is well lubricated.

The surface of the chip is serrated and of about twice the thickness of the cut. We have here evidently a case of plastic flow. The explanation of the serrations and the thickening is probably as follows:—As the tool moves into the metal, the strain gradually increases and a certain accommodation takes place due to the elasticity of the metal and the machine. When the shearing stress reaches the yield point, the metal flows, and the more rapidly as the temperature rises rapidly in the region of flow. In this process the pressure on the tool is relieved, the stress falls again below the yield point, and the process is repeated. If the machine is very sturdy with very little play, the cutting will be steadier, but here comes the advantage in the use of a good lubricant, that it is drawn into the space m, contaminates the under side of the freshly formed surface of the chip and therefore substitutes viscous flow for the energy-consuming plastic flow to a greater or less degree depending upon the efficiency of the lubricant (*cf.* Taylor, "The Art of Cutting Metals").

If the lubrication is not effective, the pressure on the tool must be relieved to a greater extent by means of plastic flow of the material. The result is greater fluctuations in pressure, the metal flowing outward during the period of flow, producing serrations of increased height, and possibly flowing downward into the space m. It is this metal, flowing inward toward the work and the point of the tool which creates the most serious condition, for it tends to break off the edge of the tool and to gouge into the face of the work.

With brittle substances such as cast iron, it is readily perceived why a lubricant is not necessary. The chip breaks as it is pried off and there is comparatively little if any plastic flow. In cutting very hard and brittle materials such as glass and some varieties of steel, a lubricant as such is not needed, but something which perhaps has just the opposite property of causing the tool to adhere to the material, *i.e.*, will cause the tool to "take hold" or "bite." Turpentine is used for this purpose on steel and turpentine with or without camphor is used on glass. It is difficult to see how these substances act

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unless they serve to remove the contaminating film of grease which is already present.

These results lead one to the observation that in difficult cases of lubrication, where seizure is always possible and is almost certain to be very disastrous, the use of pure mineral oil may not be the best practice. On the other hand, there is not enough of the fixed oils to supply the imperative demands of mankind for edible fats, soaps, leather dressing, *et cet.* Fortunately however it is likely that all of the benefit of the use of lard oil as a lubricant can be obtained very cheaply by adding to mineral oils small amounts of certain substances possessing high adhesion, particularly substances with unsaturated groups in their molecules, such as are found in oleic acid, turpentine, pine oil *et cet.* Some of these substances are already being used on a somewhat extensive scale in successful substitutes for cutting oils. The use of these substitutes opens up a field for research which is most fascinating and in view of the approaching exhaustion of our supplies of petroleum, the study is so practical that it cannot long be postponed. Of its importance we can do no better than quote from an editorial in the *Chemical Trade Journal* for December 1920: "Before the war the annual expenditure on lubricants in England was £6,000,000 and it is estimated that an annual saving of one to two millions could be effected if a systematic investigation were undertaken and the results made freely available to the public. Furthermore the loss caused by improper lubrication, would represent a very large addition to the figure given above."

Asphalt-base Versus Paraffin-base Oils.—With lubricants in use made from crude oils from different fields, the question has arisen whether the paraffin-base or the asphalt-base oil is superior, but there is a notable lack of convincing evidence in favor of either. We offer the following evidence to prove that the differences between them may be very considerable, and that the chemical composition as determined by the source of the oil is not a matter of indifference to the consumer; this is particularly true in aeroplane lubrication where the results of faulty lubrication are so very disastrous.[1]

[1] The walls of the aeroplane motor, the crankshaft *et cet.* are made so light that the seizure of a single bearing will result in the wrecking of the

Benzene (C_6H_6) represents a typical paraffin-base hydrocarbon, diallyl (C_6H_{10}) may be taken to represent an unsaturated non-cyclic hydrocarbon, whereas benzene (C_6H_6) and hexamethylene (C_6H_{12}) represent types of cyclic hydrocarbons. All of these compounds have the same number of carbon atoms, but
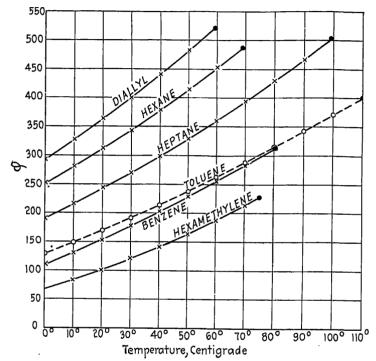
Fig. 88.—A comparison of the fluidity-temperature curves of hydrocarbons of different homologous series.

whereas their fluidity-temperature curves are nearly parallel, they are widely different as shown in Fig. 88, the fluidity of the cyclic compounds being extraordinarily low even at their boiling points, marked by large circles in the figure. The higher

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engine in mid-air, due to the sudden confining of the gas mixture within the cylinders of the engine. Flying parts of the engine resulting from such an explosion may also injure the steering mechanism, the supporting planes, or even the pilot.

fluidity of the paraffin is strikingly shown by introducing a paraffin residue (CH_3) into the benzene ring, which results in toluene (C_6H_8) having a higher fluidity than benzene (C_6H_6). On the other hand, toluene has a much lower fluidity than the purely paraffin compound heptane (C_7H_{14}) which contains the
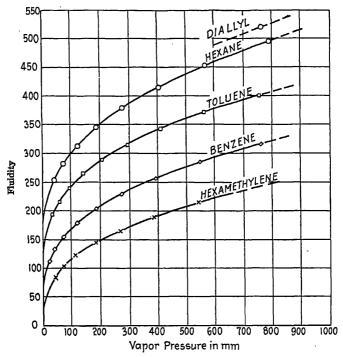
FIG. 89.—Fluidity-vapor-pressure curves of hydrocarbons of different homologous series. (*Cf.* Fig. 58.)

same number of carbon atoms. It may be urged that whereas these compounds contain the same number of carbon atoms they do not contain the same number of hydrogen atoms. But one should also note that diallyl contains more hydrogen atoms than benzene and less than hexamethylene and yet has a fluidity which is far higher than either. The cyclic compounds may owe their low fluidity to association, but the relation of association to the properties desired in a lubricant is not well understood. However, the relation between fluidity and vapor-pressure,

already discussed (pages 155–160) is not without interest in this connection.

Although hexane, diallyl, benzene, and hexamethylene differ in fluidity by more than 250 absolute units at a given temperature, they all boil within 20 degrees of each other, hence the fluidity-vapor pressure curves for these hydrocarbons are very distinctive, as shown in Fig. 89. If a low vapor pressure for a given fluidity is an advantage, on the assumption that an oil should not volatilize off from the walls of an engine cylinder or away from an overheated bearing, then straight chain hydrocarbons have the apparent advantage. On the other hand, if low vapor-pressure and high molecular weight for a given fluidity result in a tendency toward carbonization, then cyclic compounds will be preferred.

TABLE LXX.—AVERAGE FLUIDITIES AND VAPOR PRESSURES FOR CORRESPONDING TEMPERATURES

Temperature, degrees C	Toluene[1]		Benzene[2]		Hexamethylene[3]		Hexane[4]	
	φ	Vapor pressure	φ	Vapor pressure	φ	Vapor pressure	φ	Vapor pressure
0	.....	...	110.8	25.3	.....	.....	252.3	45.4
10	.....	...	131.5	45.2	84.7	47.0	281.8	75.0
20	.....	...	154.1	75.6	101.7	76.9	312.4	120.0
30	192.3	32	178.0	120.2	121.3	121.3	344.8	185.4
40	214.6	60	203.1	183.6	141.8	181.6	378.8	276.7
50	238.6	94	228.8	271.4	164.8	269.2	414.9	400.9
60	262.7	140	256.1	390.1	188.7	385.0	452.7	566.2
70	287.8	203	284.9	547.4	214.5	540.8	494.6	787.0
80	314.5	291	313.8	751.9				
90	342.8	405						
100	371.4	560						
110	400.0	751						

[1] Vapor pressure calculated from Kahlbaum, *Zeitschr. f. physik. Chem.* **26**, 603 (1898). Fluidities from Bingham and Harrison, *Zeitschr. f. physik. Chem.* **66**, 1 (1909), and in the case of hexamethylene, hitherto unpublished data of Bingham and van Klooster.

[2] From Young, *J. Chem. Soc.* (London) **55**, 486 (1889).

[3] From Young and Fortney, *J. Chem. Soc.* (London) **75**, 873 (1899).

[4] From Thomas and Young, *J. Chem. Soc.* (London) **67**, 1075 (1895).

Anti-friction Metals.—A bearing is usually made of a different material from the journal, but the composition of the so-called anti-friction metals varies within wide limits. It must be soft enough so that the bearing may be easily scraped and quickly run in to an exact fit. During the process of "running in" the bearing, the particles of metal doubtless serve to wear down the high spots of the softer metal, leaving the harder journal in a highly polished condition. The maximum wear is naturally where the journal and bearing are in closest proximity, hence if a bearing has been run in with motion in a given direction, the coefficient of friction will be altered if the direction of motion is reversed, as observed by Tower. The bearing must be hard enough to carry the load without flow of the metal. It seems probable that the material of the bearing should have as small an adhesion for the metal of the journal as practicable and in case of necessity the material of the bearing should be capable of acting as a lubricant. At any rate it should not tend to seize the journal even when molten. Ice may be regarded as the oldest anti-friction material, and from certain points of view it is ideal. Since it melts under pressure, it furnishes its own lubricant and adhesion does not occur due to pressure. A sleigh standing on moist ice may become frozen in which is evidence that adhesion is not impossible even between ice and steel. Adhesion between unlike materials is less serious however because of their different coefficients of expansion.

Tin is a common constituent of anti-friction metals and there was a serious shortage of tin during the late war. The lack of tin ores in the United States makes very desirable the knowledge of alloys which do not contain tin and at the same time are useful for bearings. Experiments indicate that lead containing a very low percentage of metallic calcium is very satisfactory.

Whether the alloy should have a certain metallographic structure, as for example, crystals of comparatively hard material imbedded in a softer amorphous solid is a moot question.

CHAPTER XII

FURTHER APPLICATIONS OF THE VISCOMETRIC METHOD

There are many further applications of the viscometric methods which are destined to become of considerable importance as soon as the theory of viscous and plastic flow is thoroughly understood. In many cases however, our knowledge at present is very restricted, or it is the closely guarded property of some industry. Generally speaking however, progress has been held back because the viscosity data at hand could not be interpreted and because the distinction between viscous and plastic flow was not recognized. An illuminating example of this has been described by Mr. Gardner and Mr. Ingalls.[1] The American Society for Testing Materials attempted to compare with all care some 240 samples of paint, applying them to a test fence at Arlington. The paints were all made up to have the same "viscosity" as measured by the Stormer viscometer. Mr. Gardner says of the tests, "The determinations were.fallacious. What was actually done was to make some paints of a very low and some of a very high yield value, although they all measured up to the same viscosity. The result was that when some of the paints were applied to the boards, they would flow and carry the pigment particles down, leaving bare spots. Some paints failed on this account."

According to Batschinski's Law the fluidity varies some 2,000 times as rapidly as the volume which is now used successfully in the dilatometric method, hence the viscometric method should be most useful in chemical control work. Dunstan, Thole and their coworkers have led the way in solving chemical problems by means of viscosity measurement. They have studied, for example, the keto-enol tautomerism, the effect of conjugate bonds, the order of chemical reactions the existence of

[1] *Proc.* A. S. T. M., **19**, Part II, (1919).

racemates in solution, the location of transition points such as the one between Na_2SO_4 and $Na_2SO_4.10H_2O$.[1] Further work along this line is needed to differentiate the effects of chemical composition, constitution, and association, measuring the fluidities over a range of temperatures. As in other lines of physical chemical investigation, the importance of making determinations at more than one temperature can hardly be overestimated because substances must be compared under conditions which are truly comparable.

Various colloidal solutions such as those of rubber, glue, viscose, nitrocellulose, dextrine, gluten, *et cet.*, offer problems of importance which can be most appropriately solved by the viscometer. It is already known that the properties of a solution of caoutchouc, for example, determine the character of the rubber which can be manufactured from it. The exact relation of the viscosity of the sol to the plasticity of the gel is practically a closed book. To indicate how complex the phenomena may be, we may add that Carl Berquist of the Corn Products Refining Company has found in an investigation of corn dextrines, tapioca dextrine, borax, gums and starches that as the percentage of dextrine increases during the process of conversion, the mobility steadily rises whereas the friction first falls, then rises, and again falls.[2] The quick setting of a gum seems to be associated with a high friction. Thus the addition of .25 per cent sodium hydroxide to a 8.33 per cent Pearl starch reduced the mobility from 0.7214 to 0.3018 but increased the friction from 108 to 156 g per square centimeter. The alkaline starch will set harder and have "better body" than an acid starch.

Nitrocellulose Solutions.—The fluidities of nitrocellulose solutions as calculated from the determinations of Baker (1913) would indicate that nitrocellulose solutions never become true solids as the percentage of nitrocellulose is increased, for the fluidities approach the zero value asymptotically. This conclusion is, however, so inherently improbable that it should be confirmed. Since it was necessary to use a series of Ostwald viscometers in order to get the necessary range, and each one is calibrated from another, the possibility of error is considerable.

[1] *Cf.* Dunstan and Langton. (1912).

[2] Privately communicated. *Cf.* Herschel and Bergquist (1921).

So it may well be that nitrocellulose solutions in various non-aqueous solvents may be brought into line with other colloidal solutions, some of which have already been considered, page 198. If, for a given nitrocellulose, there is a zero of fluidity which is independent of the particular solvent, an empirical formula of the general type

$$\varphi = \frac{\varphi_1}{10^{Kb}}$$

where K is a constant, may be serviceable, (*cf.* Duclaux and Wollman (1920)).

Colloidal solutions of the above types which have a lattice-work or sponge-like structure show an increase in the fluidity when subjected to treatment which breaks up this structure. Astonishingly small quantities of the disperse phase are necessary to give zero fluidity or at any rate a very great viscosity.

Certain non-polar emulsion colloids, such as milk, are in somewhat sharp contrast with the above, because fairly high percentages of the disperse phase alter comparatively little the fluidity of the medium and the reduction of the size of the fat gluobles by "homogenizing" decreases the fluidity.

Attempts are being made to use the plasticity method in the study and control of butter and other fats and greases. As a means for distinguishing between different fats and greases and of determining the amount of the "hardening" of oils in the process of hydrogenation, or of oxidation in the blowing of oils, the method offers opportunities which have not been exploited as yet. Similarly it seems practicable to estimate the amount or quality of gluten in samples of flour by this method.

Clay and Lime.—Suspension colloids offer a simpler set of conditions than can be found anywhere else. Clays, plasters, mortars, and cements, are all plastic and their plasticity is a matter of prime importance in their respective industries. Commenting on the influence the plasticity of plaster has on its economic usefulness, Emley (1920) states that about 70 per cent of the total cost of plastering a house is accounted for in the labor required to spread the plaster. "If one plaster is more plastic than another, it means that the plasterer can cover more square yards in a given time with the former than with the latter, which, of course, will reduce the cost. Furthermore the more

plastic material entails less physical and mental fatigue on the part of the plasterer, and he is thereby led unwittingly to produce a better quality of work."

Emley points out that the method of slaking the lime has much to do with the development of plasticity, but that quite as important is the source, and by inference, the chemical composition of the lime. A lime high in magnesium oxide is capable of developing a high plasticity more readily than one which is low in the dolomitic oxide. The growing practice of buying Ohio finishing lime, already hydrated, even when local lime may be purchased for about one-half the price is a reflection of the above facts and is a demonstration of the industrial importance of plasticity.

In handling road-building and roofing materials, a knowledge of the principles of plastic flow might enable us to avoid losses. The first principle of road building is to secure proper drainage, which is in accord with the theoretical requirement of keeping the yield value as high as practicable. The "metal" of the railroad is made up of coarse crushed stone of uniform size which gives excellent drainage and a very high yield point. Where liquid hydrocarbons are used as binder, a considerable amount of fine material must be used in order to raise the yield point sufficiently to sustain the contemplated loads. In order to be able to apply the material the mobility is greatly increased by raising the temperature.

Paints and Pigments.—Paint must have a yield value high enough so that it will not run under the influence of gravity but the mobility must also be high so that the painter may spread it without undue fatigue. Other things being equal, these ends are both achieved by the use of finely-divided materials, and at the same time the covering power is augmented. Perrott (1919) has made a study of the plasticity of "long" and "short" carbon blacks.

Up to 1914, Austrian ozokerite was thought to be essential in the wax used in making electrotypes. Research has shown that a good impression can be obtained and held with waxes which do not contain the Austrian material.

Textiles and Belting.—If a cotton window cord is run over a free pulley a certain number of times under a load which is small in comparison with the tensile strength of the cord, it may fail

while another cord, apparently no better as judged by the weight, tensile strength, method of fabrication and length of staple will last perhaps one hundred times as long. It is evident that oxidation or decay cannot play an important part because the failure may be brought about in a few hours. It is not due to friction of the pulley as the pulley in all cases is running free. The surprising thing about it is that the cord often wears out on the side which is away from the pulley, or the center of the cord may become completely pulverized while the outside is apparently sound.

An analysis of what happens when a belt moves over a pulley shows that the outside of the belt moves along a longer arc and therefore tends to get ahead of the inside of the belt. There is consequently a shearing stress set up within the belt. Since the individual fibers are comparatively weak, it is of the utmost importance that the individual fibers be protected from undue strains. In order to obtain relief where the strains are greatest, a lubricant between the fibers and plies should always be provided. A rosined bow adheres to a violin string and in the production of sweet sound accumulates stresses advantageously, but the workman who gets rosin on a machine belt with the idea of gaining greater traction, may quickly bring about the destruction of the belt. A certain amount of slipping of a belt and particularly in the belt is necessary and desirable.

Lard and certain fixed oils are used to "stuff" leather, and a good leather belt will practically never wear out if well-used and dressed with lubricant occasionally. Window cords are often lubricated with a soft paraffin. The paraffin has a tendency to work out in use and since it becomes hard at low temperatures, it then tends to make the cord stiff. Pitch and its congeners is unsuitable for use on textile belting due to its having a high temperature coefficient of fluidity. What is needed as a lubricant is a substance which adheres strongly to the material, lubricates the fibers, and has a small or negligible temperature coefficient of fluidity. Oils which serve well with leather will not fill the coarser pores of textile belting, hence rubber, balata, and semi-drying oils are often used. In ordinary fabrics a certain amount of oil present will add to their life. Even a wire rope will last longer if there is lubricant between the strands.

Metallurgy.—The terms hardness, ductility, pliability, malleability are terms which are probably, like the term plasticity, complex in character and may in time come to be more precisely defined in terms of friction and mobility. It is desirable to know the friction and mobility of each modification of each metal and their several alloys, and also the effect upon these properties of changes in crystal size or shape and in the amount of amorphous solid between the crystals. This subject merits extended treatment. We know that annealing gives the crystals opportunity to develop whereas cold working tends to break up the crystal structure and thereby toughens the metal. Quenching the hot metal of course prevents crystal growth and should decrease the yield point. There is no doubt but that polishing and similar operations result in a plastic flow of the surface layers of a metal.

Biology, Medicine and Pharmacy.—It would be out of place here to treat in detail of the very numerous papers which have been devoted to biological subjects. Beginning with Poiseuille who was first drawn to his study of fluidity through his interest in the circulation of the blood in the capillaries, there has been a continued interest in the viscosities of animal liquids. The viscosity of the blood in various individuals and species of animals, in various pathological conditions as well as under the influence of anaesthetics and drugs, the effect on viscosity caused by differences in diet, age, sex, or temperature outside of the body, the effect upon the viscosity of the blood produced by the removal of certain organs of the body have all been subject to investigation. The composite character of the blood has prompted inquiries in regard to the viscosity of blood serum and defibrinated blood as compared either with blood as it exists within the animal or as it is freshly drawn. The other body fluids, milk, lymph, perspiration, the vitreous humor, *et cet.*, have all been studied and carefully reviewed by Rossi (1906).

Rossi finds that preceding the coagulation of a solution there is an increase in viscosity which is the best measure of the progress toward coagulation. The more viscous the original solution, the more rapidly does the formation of the gel proceed. Fano and Rossi (1904) found that electrolytes always first cause a drop in the viscosity which is then followed by a rise as the concentration

is increased. All liquids in the body, whether circulating or not have the minimum viscosity compatible with their colloidal content.

Oxygenated blood according to Haro (1876) is much more fluid than blood through which carbon dioxide has been made to bubble, the ratio between them being 5.61 to 6.08. Mere physical solutions of small amounts of gases in liquids usually affect the fluidity but imperceptibly, but the data on this subject needs amplification. Ether and ethyl alcohol added to the blood increase its fluidity, whereas chloroform has the opposite effect.

Poiseuille compared the rates of flow of blood serum through glass tubes and through a given vascular territory varying the viscosity of the serum by various additions. From the correlation it has been assumed that the laws of Poiseuille apply to the flow of blood through the capillaries of the body. Ewald (1877) has questioned this conclusion and Huebner (1905) has noted an incongruity in the rate of flow of solutions of known viscosity in the organs of a frog. When blood flows through the capillaries the corpuscles are deformed and the capillaries are more or less elastic. The problems connected with the viscosity of the blood are complicated by the fact that the fibrinogen of the blood in contact with foreign substances produces coagulation which may produce a coating on the inside of the tubes. Lewy (1897) however has found that Poiseuille's law holds good so long as no sedimentation takes place, hence the more viscous the blood the longer it will take to diffuse through a given vascular territory.

Burton-Opitz (1914) found that fasting produced a pronounced increase in the fluidity of the blood of a dog. A meat diet has the greatest effect in lowering the fluidity, a fat diet next, and a diet of carbohydrates least of all. The fluidity of the serum varies in a manner similar to that of the blood in these particular experiments.

Bleeding a dog causes the fluidity of the blood to decrease. When a dog was kept in a bath at 43°C the fluidity of the blood increased, and it decreased when the temperature of the bath was lowered to 23°, the most rapid change taking place in from 5 to 15 minutes according to Huerthle (1900).

According to Huebner the red blood corpuscles account for

from two-thirds to three-quarters of the viscosity of the blood. The fluidity of the blood of cold-blooded animals is higher than that of warm-blooded animals, but the rabbit is peculiar among warm-blooded animals in having blood of exceptionally high fluidity.

Milk.—The fluidity of the milk of a cow differs from day to day as well as with different individuals and at different periods of life. The fluidity of woman's milk is highest directly after childbirth and falls off nearly 50 per cent during the period of nursing. The milk of goats is less fluid than that of cows. According to Cavazzani (1905) the addition to milk of small amounts of NaOH or KOH produces a change in the fluidity of the milk of a cow, goat, or horse but does not affect the fluidity of woman's milk. According to Alexander[1] human milk contains a protective colloid not present in cow's milk, hence coarse curds are not formed on adding acids.

The action of ferments upon milk has been studied by Gutzeit (1895) and Fuld (1902). The decline in the viscosity of a solution of proteins during digestion by means of trypsin has been the subject of study by Spriggs (1902). The greater part of the loss in viscosity occurs considerably before the completion of the digestion, according to Bayliss (1904). This is in accordance with the idea that the destruction of the structure must lower the viscosity tremendously, whereas the splitting of microscopic particles may increase the viscosity and the splitting of amicroscopic particles decreases the viscosity. Spriggs (1902) and Zanda (1911) investigated the changes in viscosity during digestion by pepsin.

Ceramics and Glass Making.—The thorough mixing of glass melts, the removal of bubbles of gases, and the pressure necessary to blow the glass at a given temperature all depend upon the fluidity of the melt, hence the control of the fluidity of glass melts is of importance.

The Seger cone method of determining temperatures suggests the possibility of measuring high temperatures by the viscometric method. Barus proposed to use the viscosity of a gas for this purpose.

The manufacture of porcelain is concerned with the principles

[1] *J. Soc. Chem. Ind.* **28**, 280 (1909).

of plastic flow at every stage. Clays must have a friction high enough so that the ware will not lose its shape while in the moist condition and at the same time it must have a mobility which is high enough so that the clay may be readily worked and it must not shrink badly on drying. On heating, the more fusible particles must soften sufficiently to weld the particles together, but again the friction must be sufficient so that there will be no serious loss of shape. When the glaze is added, it must fill the pores quickly and yet not "run." So many problems in plastic flow seem to call for precise control of conditions in order to avoid large losses.

It is found that considerable amounts of non-plastic clay, fine sand, or ground porcelain (grog) may be added to a very plastic clay without greatly lowering its plasticity. Until more data is accumulated, this may remain something of a mystery, but these additions are valuable and probably serve somewhat the function of the "reinforcing" in concrete or of the colloid in "solidified alcohol."

Geo-physics.—Basic lavas are notably fluid as compared with acidic lavas which are more viscous. This has important bearings upon the character of volcanic eruptions in different parts of the world and presumably therefore upon the past history of the earth. For example, the Hawaiian volcanoes with a highly basic lava tend to remain open, flow quietly, build a low-angle cone, the lava spreading out over a large amount of territory. On the other hand, the Mexican volcanoes with acidic lava are apt to harden over during quiescence and then erupt violently. A low-angle cone is impossible. In accordance with the relationship between the fluidity of the melt and the rate of crystallization, we should expect to find the basic lavas more coarsely crystalline than those of a more acidic nature. The length of time required for an obsidian to take on a cryptocrystalline, microcrystalline or even macrocrystalline character will of course also depend upon the temperature and to a lesser extent upon the pressure as well as the chemical composition, for all of these factors influence the fluidity. Silicate melts have been studied by Doelter (1906).

Segregations, as in the separation of iron from slag, is dependent to a certain extent upon the fluidity of the slag and of the

molten metal. Feild (1918) has investigated the viscosity of slags.

The sodium silicate used in industry contains varying hydroxyl ion concentration. An excess of silicic acid increases the adhesiveness but lowers the mobility. Excess of alkali has the opposite effect. The alkalinity of sodium silicate is therefore obviously an important control factor.

Conclusion.—If one plots the viscosity-concentration curves of a colloid sol of the type of gelatine in water or of nitrocellulose in acetone, one finds that the viscosity rapidly goes from the very small viscosity of the pure solvent ($0.01p$ for water at 20° and 0.003 for acetone at 25°) to an extremely high value which may be regarded as infinite, in a concentration of only a few per cent. Plotting these curves leads to unsatisfactory results, which need not be exhibited here as they are very common in the literature; the curves fall together at one extreme as soon as one tries to represent more than the most dilute solutions, and whereas they may or may not coincide at the other extreme, we can form no idea of what happens since that extreme is infinitely removed from us.

If however we plot fluidities instead of viscosities the whole problem becomes immediately simplified, for the fluidities of the pure solvents assume their proper importance and the fluidity goes to or, at any rate, approaches zero, which is accessible. Moreover the concentration of zero fluidity has a definite and important significance. If the relation turns out to be also linear, then the problem is one of ideal simplicity.

To go over all of the data in the literature, critically examining the data to see how far it could be used to support and further amplify the theories set forth in this work has been a pleasant task but far too great for a single worker. Already several workers are in the field and in the Index and Appendix I are bringing together a considerable number of references and tables in order to facilitate the work.

A consideration of the following data may aid any who are interested in the theoretical study of colloids or in their industrial applications, since they help us to answer the very important and novel questions: "Are fluidity-temperature curves linear in the case of emulsoid colloids of the type of gelatine?" "Are their

fluidity-concentration curves linear?" and "Does the fluid 'sol' pass into the plastic 'gel' at a perfectly definite concentration and temperature?"

Arisz (1915) has made a valuable study of the viscosity of a 10 per cent gelatine sol in a glycerol-water mixture of 1.175 specific gravity, with changing temperatures. Calculating the fluidities, we obtain the linear curve

$$\varphi = 0.000227 \, (t - 45.2) \tag{112}$$

which represents faithfully the observed values of the fluidities given in Table LXXI. The temperature of zero fluidity is a little over 45°, which must therefore be regarded as the transition point between the fluid and solid phases, *i.e.*, the melting-point.

TABLE LXXI.—THE FLUIDITIES OF 10 PER CENT GELATINE SOLUTION IN GLYCEROL-WATER MIXTURE OF DIFFERENT TEMPERATURES (AFTER ARISZ)

Temperature, degrees	Viscosity, observed	Fluidity, observed	Fluidity, calculated
44	30,000	0.000003	0.0000
46	5,000 ±	0.00020 ∓	0.0002
47	4,200 −	0.00024 +	0.0004
50	950 ±	0.00105 ∓	0.0011
55	415	0.0024	0.0022
65	222	0.0045	0.0045

In considering the effect of concentration on fluidity, we cite first the data of Lüers and Schneider (1920) on flour-water mixtures for 20°, giving the concentrations in volume percentages $(100b)$ and changing the viscosities to fluidities, Table LXXII. The fluidities are again faithfully reproduced by means of a linear formula, *viz.*,

$$\varphi = 100.5 - 569.6b \tag{113}$$

except the last two concentrations, where the observed fluidity is too high. This gives a concentration of zero fluidity as 17.6 per cent, which corresponds to the transition from viscous to plastic flow. This is very close to the concentrations of zero fluidity found by Bingham (1916) for clay suspensions, page 229.

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TABLE LXXII.—THE FLUIDITIES OF VARIOUS VOLUME CONCENTRATIONS
OF MALT FLOUR-WATER MIXTURES AT 20°C (AFTER LÜERS AND
SCHNEIDER)

1 g flour displaces 0.6766 ml of toluene

Volume, per cent	Viscosity relative, observed	Fluidity absolute, observed	Fluidity absolute, calculated
0.000	1.000	100.5	100.5
0.338	1.010	99.5	98.6
0.676	1.042	96.5	96.6
1.352	1.090	92.2	92.8
2.704	1.192	84.3	85.1
5.408	1.433	70.1	69.7
8.120	1.844	54.5	54.2
10.816	2.566	39.2	38.9
13.520	3.459	29.0	23.5
16.240	4.839	20.8	8.0

There are certain cases where the fluidity-concentration relation is not linear as in case of Baker's data for nitrocellulose solutions. It seems unwise to make any sweeping deductions in regard to the meaning of these curves until they are confirmed by further observations, for it is possible that correction terms applied to the measurements might serve to rectify the curves. It is perhaps needless to add that if the curvature is real, it will have an important bearing upon the nature of colloids. I am engaged upon a study of this whole matter at the present time.

In a few cases, of which one has been already cited, page 207, the fluidity curve consists of two linear branches, meeting at a sharp angle. This would seem to indicate a transition point, but in view of the uncertainties connected with the measurements of the viscosities of colloidal solutions, we may be pardoned for extreme caution in making such an assumption until the real existence of such a singular point has been thoroughly verified. Such a singular point is found for example in the data for aqueous solutions of sodium palmitate at 70°C as determined by Farrow (1912). The formula

$$\varphi = 240.4 - 503.9 b_W \tag{114}$$

represents the relation between the fluidity and the weight

centration up to a concentration of 0.175 but this and the remaining observations are reproduced by the formula

$$\varphi = 207.7 - 306.7b_W \qquad (115)$$

Neither formula gives the true fluidity of water at 70° (245.7) when the weight concentration b_W of palmitate is zero, and we obtain two different concentrations corresponding to zero fluidity, using the two formulas, of 0.477 and 0.677 respectively, which are difficult to interpret.

TABLE LXXIII.—FLUIDITIES OF AQUEOUS SOLUTIONS OF SODIUM PALMITATE AT 70°C (AFTER FARROW)
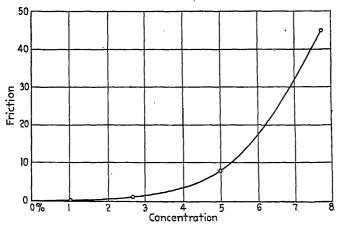
Concentration by weight	Viscosity, observed	Fluidity, observed	Fluidity, calculated	
0.026	0.00438	228	227	
0.064	0.00485	206	208	
0.105	0.00530	189	188	
0.131	0.00579	173	174	Formula I
0.141	0.00592	169	169	
0.175	0.00647	155	152	
0.175	0.00647	155	154	
0.187	0.00665	150	150	
0.232	0.00743	135	136	
0.283	0.00793	126	121	
0 287	0.00866	115	120	
0.293	0.00847	118	118	Formula II
0.302	0.00886	113	115	
0.329	0.00949	105	107	
0.380	0.01113	90	91	
0.451	0.01363	73	69	
0.499	0.01800	56	55	

W. L. Hyden has made a study of the plasticity of solutions of nitrocellulose in acetone, but the results have not yet been published. He finds that these colloidal solutions differ from the suspensions of clay *et cet.* studied by Durham in that the concentration of zero fluidity at a very low shear, *i.e.*, the transition from viscous to plastic flow, occurs in an extraordinarily low concentration of colloid, certainly less than one per cent.

Since the apparent viscosity of such colloid solutions is depen-

dent upon the amount of the shearing force, the values of the
viscosity as such are quite illusory. For example, a 1.39 per
cent solution of nitrocellulose in acetone gave a fluidity of
52.49 using a pressure of 403.6 g per cm² whereas the fluidity
apparently fell to 51.31 at 214.5 g per cm² and to 50.76 at 62.96
g per cm². These results are similar to those of Glaser (*cf.*
Table XVIII).

It is quite possible to measure the plasticity of materials of
this kind in the viscometer shown in Fig. 29. It is merely
necessary to measure the flow at two or more pressures and then

FIG. 90.—Friction-weight-concentration curve for colloidal dispersions of
nitrocellulose in acetone measured in dynes per square centimeter.

compare the volume of flow with the shearing stress. The
volume of flow-shearing stress curves obtained in this way by
Hyden are linear in every case. The mobility is found to in-
crease with the temperature in a nearly linear manner and the
mobility falls off very rapidly with increasing concentration of
colloid, approaching the zero value asymptotically. Both of these
results are similar to those for clay suspensions (*cf.* pages 220
and 221). The equations of these curves have not yet been
obtained.

The friction in nitrocellulose solutions increases rapidly with
increasing concentration of colloid, as shown in Fig. 90. As the
temperature is raised the friction is decreased in a linear manner,

Fig. 91, so that at about 43°C nitrocellulose in acetone would appear to have the properties of a true fluid. If above 43° we have a true solution, this temperature is a transmission point which is analogous to the melting point of a solid. This does not mean however that there would be any marked change in the working properties as nitrocellulose solutions below 43° are extremely soft solids.
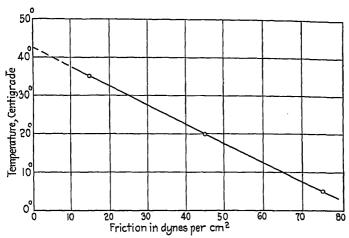
Fig. 91.—Temperature-friction curve for a colloidal dispersion of 7.708 weight percentage of nitrocellulose in acetone.

Solubility and Plasticity.—It is of course well-known that the so-called "solutions" of nitrocellulose, gelatine and other colloids are not true solutions, nevertheless the term solution as applied to colloidal dispersions often leads to confusion. Thus acetone is one of the best "solvents" for nitrocellulose, being superior to let us say, amyl acetate. But what does this statement mean? It cannot possibly mean that acetone will actually dissolve more nitrocellulose than will a similar amount of amyl acetate, for there is no point of saturation for either, *i.e.*, both liquids will "dissolve" or better disperse an indefinite amount of colloid; hence the term *solubility* has here a very special, albeit a very definite, meaning, *viz.*, that dispersive medium is the best solvent which with a given amount of colloid gives an emulsion having the maximum mobility. Here however there enters the

fact, which seems from the literature not to have been sufficiently considered, that acetone has a far greater fluidity than amyl acetate to start with, and this must of necessity affect the mobility of dispersions in these media. It is evident that this must be taken into account if we are to get a true measure of the dispersive power of different media. This work is being continued.

APPENDIX A

PRACTICAL VISCOMETRY

The most essential part of the viscometer is shown in Fig. 29, p. 76. To use the apparatus an appropriate amount of the liquid whose viscosity is to be measured is pipetted into the right limb. The liquid at the desired temperature is forced over into the left limb until the right meniscus reaches the point N, it being noted that there is sufficient liquid so that the surplus runs over into the trap. The right limb is turned to air so as to prevent more liquid from flowing into the trap. Having adjusted the working volume, the left limb is connected with the pressure, and the time required for the left meniscus to fall from B to D is noted. The left limb is now turned to atmospheric pressure and the instrument is ready for an immediate duplicate determination in the opposite direction. In this second measurement the time is noted which is required for the left meniscus to rise from D to B.

Knowing the pressure, p in grams per square centimeter, the time, t, in seconds, the two constants of the instrument, C and C', and the density of the liquid, ρ, the viscosity η at the given temperature is given by the formula, (cf. p. 74).

$$\eta = Cpt - C'\rho/t \tag{1}$$

DETERMINATION OF THE CONSTANTS OF THE INSTRUMENT

The second term of the right hand member of the above equation is the kinetic energy correction which should never exceed 5 per cent of the value of the first term. For this reason the value of the constant C' and of the density ρ need be known with an accuracy of 2 per cent only in order to allow viscosity determinations to be made with an error of only one-tenth of 1 per cent.

$$C' = 0.0446V/l \tag{2}$$

where V is the volume in milliliters of the bulb C between the marks B and D, and l is the length of the capillary EF, log. $0.0446 = 8.64895 - 10$.

The value of the constant C is most conveniently obtained by filling the instrument with freshly distilled, dust-free water and determining the time of flow for each limb, at 20°C.

$$C = \frac{0.01005t + C'\rho}{pt^2} \tag{3}$$

for water at 20°. This constant may also be obtained by direct measurement

$$C = 384.8r^4/Vl \tag{4}$$

where r is the radius of the capillary in centimeters. If the acceleration of gravitation of the locality is not 980, the value of C must be increased 0.1 per cent for each unit in excess.

Since the bulbs C and K may differ in level, it is evident that the pressure, p, used in calculating the viscosity is not necessarily equal to the pressure, p_1, delivered by the compressed air at the top of the viscometer. If the bulb K is higher than the bulb C by a distance h, then it is evident that the pressure during the left limb determination is decreased by an amount $h_1\rho$ and the pressure during the right limb determination is increased by the same amount. Hence,

$$p_1 - h_1\rho = \frac{\eta + C'\rho/t_1}{C_1 t_1} \text{ (left limb)}$$

$$p_2 + h_1\rho = \frac{\eta + C'\rho/t_2}{C t_2} \text{ (right limb)}$$

and therefore

$$h_1 = \frac{\eta}{2C\rho}\left(\frac{1}{t_1} - \frac{1}{t_2}\right) + \frac{C'}{2C}\left(\frac{1}{t_1^2} - \frac{1}{t_2^2}\right) - \frac{p_2 - p^1}{2}$$

or if the two determinations are carried out with water at 20° using the same pressure

$$h_1 = \frac{0.005034}{C}\left(\frac{1}{t_1} - \frac{1}{t_2}\right) + \frac{C'}{2C}\left(\frac{1}{t_1^2} - \frac{1}{t_2^2}\right) \tag{5}$$

where t, is the time of flow from right to left and t_2 is the time of flow from left to right. Log. $0.005034 = 7.70191 - 10$.

The value of C used in calculating the hydrostatic head is an approximate value obtained from Eq. (3) by employing the pressure, p_1, uncorrected for hydrostatic head, which is legitimate since the hydrostatic head is at the most only a small correction term.

J. W. Temple has worked out a simpler method for calculating

the hydrostatic head when the flow in opposite directions is carried out at the same manometer pressure p. Let the time of flow in the one direction t_L, under the true pressure corrected for hydrostatic head $p_L = p + h_1\rho$, be supposed to be less than the time t_R in the opposite direction under the pressure $p_R = p - h_1\rho$. Then

$$h_1 = \frac{p_L - p_R}{2\rho}$$

and substituting into this equation the values of p_L and p_R given by Eq. (1), we have

$$h_1 = \frac{1}{2\rho}\left(\frac{\eta + C'\rho/t_L}{Ct_L} - \frac{\eta + C'\rho/t_R}{Ct_R}\right)$$

but in the kinetic energy correction, which is itself always small, the small hydrostatic head correction is of negligible influence, hence for our purpose we may write $\eta + C'\rho/t_L = \eta + C'\rho/t_R$ so

$$h_1 = \frac{1}{2C\rho}\cdot\frac{t_R - t_L}{t_L t_R}\left(\eta + C'\rho/t_L\right)$$

but from Eq. (1) we have that $\eta + C'\rho/t_L = Cp_L t_L$ hence

$$h_1 = \frac{p_L}{2\rho}\cdot\frac{t_R - t_L}{t_R} \tag{6}$$

The True Average Pressure

It might inadvertently be assumed that if the two bulbs C and K are the same in shape and volume and also at the same level, the true pressure to be used in calculating the viscosity would necessarily be the pressure p_1 delivered by the compressed air in the viscometer because the hydrostatic head as obtained above would then be zero. But since the hydrostatic head in the viscometer is really continually changing, the true average pressure may not be zero under the above conditions, and it must be obtained by integration. Bingham, Schlesinger, and Coleman (1916)[1] have shown that for cylindrical bulbs the true average pressure p would be

$$p = \frac{0.8686h\rho}{\log_{10}\dfrac{p_0 + h\rho}{p_0 - h\rho}} \tag{7}$$

[1] For other shapes of bulbs see original paper of Bingham, Schlesinger, and Coleman. For the possible importance of such corrections see Kendall and Munroe (1917).

where h is the height of the bulb and p_0 is the pressure with all other corrections made. Fortunately if the height of the bulb BD, in Fig 29, is not more than one-thirtieth of the whole pressure, this correction is unnecessary to attain the desired accuracy of 0.1 per cent.

In any case, however, the student should determine by experiment whether a change in manometer pressure is without effect upon the valve of C.

The Pressure Corrections Outside the Viscometer

Let the density of the liquid within the manometer be ρ_0 at a temperature T in degrees Centigrade and the height read on the manometer scale—corrected for scale error if necessary—be h_0; also let the viscometer bulbs be at a height h' above the middle point of the manometer. The pressure delivered to the air in the viscometer becomes

$$p_1 = h_0 - K \pm L \text{ for a water manometer} \tag{8}$$

$$p_1 = M \pm N \text{ for a mercury manometer} \tag{9}$$

where the values of L are given in Table I and may be made entirely negligible in the setting up of the apparatus.

Table I.—Values of L

h' in centimeters	h_0 in centimeters		
	100	200	300
50	0.01	0.01	0.02
100	0.01	0.03	0.04
200	0.03	0.05	0.08
300	0.04	0.08	0.11

The values of K are given in Table II.

TABLE II.—VALUES OF K

Temperature, degrees centigrade	Manometer reading, h_0											
	10	20	30	40	50	60	70	80	90	100	200	300
5	0.013	0.025	0.039	0.053	0.066	0.079	0.094	0.108	0.122	0.136	0.285	0.482
10	0.016	0.030	0.046	0.064	0.078	0.095	0.112	0.129	0.145	0.162	0.337	0.533
11	0.017	0.032	0.050	0.068	0.083	0.101	0.119	0.137	0.154	0.172	0.357	0.563
12	0.018	0.035	0.053	0.072	0.089	0.108	0.126	0.145	0.163	0.183	0.379	0.596
13	0.019	0.037	0.057	0.077	0.095	0.115	0.135	0.155	0.175	0.195	0.403	0.632
14	0.020	0.040	0.061	0.082	0.102	0.123	0.144	0.165	0.187	0.208	0.429	0.671
15	0.022	0.043	0.065	0.088	0.110	0.131	0.154	0.177	0.199	0.222	0.457	0.713
16	0.023	0.046	0.070	0.094	0.118	0.140	0.165	0.189	0.212	0.238	0.489	0.761
17	0.025	0.049	0.075	0.101	0.126	0.150	0.176	0.203	0.228	0.255	0.523	0.812
18	0.027	0.053	0.080	0.108	0.135	0.161	0.189	0.217	0.245	0.273	0.559	0.866
19	0.029	0.057	0.086	0.116	0.144	0.173	0.203	0.233	0.262	0.292	0.597	0.923
20	0.031	0.060	0.092	0.124	0.154	0.185	0.217	0.249	0.280	0.312	0.637	0.983
21	0.033	0.065	0.098	0.132	0.165	0.198	0.232	0.265	0.299	0.333	0.679	1.046
22	0.035	0.069	0.105	0.141	0.176	0.211	0.247	0.282	0.319	0.355	0.723	1.113
23	0.037	0.074	0.112	0.151	0.188	0.225	0.264	0.301	0.341	0.379	0.770	1.184
24	0.040	0.079	0.119	0.160	0.200	0.240	0.281	0.321	0.363	0.403	0.819	1.256
25	0.042	0.084	0.127	0.170	0.212	0.255	0.298	0.341	0.385	0.428	0.869	1.331
26	0.045	0.089	0.135	0.181	0.225	0.270	0.316	0.362	0.408	0.454	0.921	1.409
27	0.048	0.094	0.143	0.191	0.239	0.286	0.335	0.383	0.432	0.481	0.975	1.490
28	0.050	0.100	0.151	0.202	0.253	0.303	0.355	0.405	0.458	0.509	1.031	1.574
29	0.053	0.105	0.160	0.214	0.268	0.321	0.375	0.429	0.484	0.538	1.089	1.661
30	0.056	0.111	0.169	0.226	0.283	0.339	0.396	0.453	0.511	0.568	1.149	1.751
31	0.059	0.117	0.178	0.239	0.298	0.357	0.417	0.478	0.538	0.599	1.210	1.842
32	0.062	0.124	0.188	0.251	0.314	0.376	0.439	0.503	0.567	0.630	1.273	1.937
33	0.066	0.130	0.197	0.264	0.330	0.395	0.462	0.529	0.595	0.662	1.337	2.033
34	0.069	0.137	0.207	0.277	0.346	0.415	0.485	0.555	0.625	0.695	1.403	2.132

If the pressure is read on a mercury manometer at 20°, the heights in mercurial centimeters may be converted into grams per square centimeter by means of Table III.

TABLE III.—VALUES OF M. PRESSURES IN GRAMS PER SQUARE CENTIMETER, FOR HEIGHTS IN MERCURIAL CENTIMETERS

Height, centimeters of mercury	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
10	135.4	36.8	38.2	39.5	40.9	42.2	43.6	44.9	46.3	47.6
11	49.0	50.3	51.7	53.1	54.4	55.8	57.1	58.5	59.8	61.2
12	62.5	63.9	65.2	66.6	68.0	69.3	70.7	72.0	73.4	74.7
13	76.1	77.4	78.8	80.1	81.5	82.9	84.2	85.6	86.9	88.3
14	89.6	91.0	92.3	93.7	95.0	96.4	97.8	99.1	*00.5	*01.8
15	203.2	04.5	05.9	07.2	08.6	09.9	11.3	12.7	14.0	15.4
16	16.7	18.1	19.4	20.8	22.1	23.5	24.8	26.2	27.6	28.9
17	30.3	31.6	33.0	34.3	35.7	37.0	38.4	39.7	41.1	42.5
18	43.8	45.2	46.5	47.9	49.2	50.6	51.9	53.3	54.6	56.0
19	57.4	58.7	60.1	61.4	62.8	64.1	65.5	66.8	68.2	69.5
20	70.9	72.2	73.6	75.0	76.3	77.7	79.0	80.4	81.7	83.1
21	84.4	85.8	87.2	88.5	89.9	91.2	92.6	93.9	95.3	96.6
22	98.0	99.3	*00.7	*02.0	*03.4	*04.8	*06.1	*07.5	*08.8	*10.2
23	311.5	12.9	14.2	15.6	16.9	18.3	19.7	21.0	22.4	23.7
24	25.1	26.4	27.8	29.1	30.5	31.8	33.2	34.6	35.9	37.3
25	38.6	40.0	41.3	42.7	44.0	45.4	46.7	48.1	49.5	50.8
26	52.2	53.5	54.9	56.2	57.6	58.9	60.3	61.6	63.0	64.4
27	65.7	67.1	68.4	69.8	71.1	72.5	73.8	75.2	76.5	77.9
28	79.2	80.6	82.0	83.3	84.7	86.0	87.4	88.7	90.1	91.4
29	92.8	94.2	95.5	96.9	98.2	99.6	*00.9	*02.3	*03.6	*05.0
30	406.3	07.7	09.1	10.4	11.8	13.1	14.5	15.8	17.2	18.5
31	19.9	21.2	22.6	24.0	25.3	26.7	28.0	29.4	30.7	32.1
32	33.4	34.8	36.1	37.5	38.9	40.2	41.6	42.9	44.3	45.6
33	47.0	48.3	49.7	51.0	52.4	53.7	55.1	56.5	57.8	59.2
34	60.5	61.9	63.2	64.6	65.9	67.3	68.6	70.0	71.4	72.7
35	74.1	75.4	76.8	78.1	79.5	80.8	82.2	83.5	84.9	86.3
36	87.6	89.0	90.3	91.7	93.0	94.4	95.7	97.1	98.4	99.8
37	501.2	02.5	03.9	05.2	06.6	07.9	09.3	10.6	12.0	13.3
38	14.7	16.1	17.4	18.8	20.1	21.5	22.8	24.2	25.5	26.9
39	28.2	29.6	31.0	32.3	33.7	35.0	36.4	37.7	39.1	40.4
40	41.8	43.1	44.5	45.9	47.2	48.6	49.9	51.3	52.6	54.0
41	55.3	56.7	58.0	59.4	60.8	62.1	63.5	64.8	66.2	67.5
42	68.9	70.2	71.6	72.9	74.3	75.6	77.0	78.4	79.7	81.1
43	82.4	83.8	85.1	86.5	87.8	89.2	90.5	91.9	93.3	94.6
44	96.0	97.3	98.7	*00.0	*01.4	*02.7	*04.1	*05.4	*06.8	*08.2
45	609.5	10.9	12.2	13.6	14.9	16.3	17.6	19.0	20.3	21.7
46	23.1	24.4	25.8	27.1	28.5	29.8	31.2	32.5	33.9	35.2
47	36.6	38.0	39.3	40.7	42.0	43.4	44.7	46.1	47.4	48.8
48	50.1	51.5	52.9	54.2	55.6	56.9	58.3	59.6	61.0	62.3
49	63.7	65.0	66.4	67.8	69.1	70.5	71.8	73.2	74.5	75.9
50	77.2	78.6	79.9	81.3	82.6	84.0	85.4	86.7	88.1	89.4
51	90.8	92.1	93.5	94.8	96.2	97.5	98.9	*00.3	*01.6	*03.0
52	704.3	05.7	07.0	08.4	09.7	11.1	12.4	13.8	15.2	16.5
53	17.9	19.2	20.6	21.9	23.3	24.6	26.0	27.3	28.7	30.1
54	31.4	32.8	34.1	35.5	36.8	38.2	39.5	40.9	42.2	43.6
55	45.0	46.3	47.7	49.0	50.4	51.7	53.1	54.4	55.8	57.1
56	58.5	59.9	61.2	62.6	63.9	65.3	66.6	68.0	69.3	70.7
57	72.0	73.4	74.7	76.1	77.5	78.8	80.2	81.5	82.9	84.2
58	85.6	86.9	88.3	89.6	91.0	92.4	93.7	95.1	96.4	97.8
59	99.1	*00.5	*01.8	*03.2	*04.5	*05.9	*07.3	*08.6	*10.0	*11.3
60	812.7	14.0	15.4	16.7	18.1	19.4	20.8	22.2	23.5	24.9
61	26.2	27.6	28.9	30.3	31.6	33.0	34.3	35.7	37.1	38.4
62	39.8	41.1	42.5	43.8	45.2	46.5	47.9	49.2	50.6	52.0
63	53.3	54.7	56.0	57.4	58.7	60.1	61.4	62.8	64.1	65.5
64	66.8	68.2	69.6	70.9	72.3	73.6	75.0	76.3	77.7	79.0
65	80.4	81.7	83.1	84.5	85.8	87.2	88.5	89.9	91.2	92.6
66	93.9	95.3	96.6	98.0	99.4	*00.7	*02.1	*03.4	*04.8	*06.1
67	907.5	08.8	10.2	11.5	12.9	14.3	15.6	17.0	18.3	19.7
68	21.0	22.4	23.7	25.1	26.4	27.8	29.2	30.5	31.9	33.2
69	34.6	35.9	37.3	38.6	40.0	41.3	42.7	44.1	45.4	46.8

Marginal proportional-parts table:

	1.4
0.1	0.1
0.2	0.3
0.3	0.5
0.4	0.6
0.5	0.7
0.6	0.8
0.7	1.0
0.8	1.1
0.9	1.3

Table III.—*Continued*

Height, centimeters of mercury	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
70	48.1	49.5	50.8	52.2	53.5	54.9	56.2	57.6	58.9	60.3
71	61.7	63.0	64.4	65.7	67.1	68.4	69.8	71.1	72.5	73.8
72	75.2	76.6	77.9	79.3	80.6	82.0	83.3	84.7	86.0	87.4
73	88.7	90.1	91.5	92.8	94.2	95.5	96.9	98.2	99.6	*00.9
74	1002.3	03.6	05.0	06.4	07.7	09.1	10.4	11.8	13.1	14.5
75	15.8	17.2	18.5	19.9	21.2	22.6	24.0	25.3	26.7	28.0
76	29.4	30.7	32.1	33.4	34.8	36.1	37.5	38.9	40.2	41.6
77	42.9	44.3	45.6	47.0	48.3	49.7	51.0	52.4	53.8	55.1
78	56.5	57.8	59.2	60.5	61.9	63.2	64.6	65.9	67.3	68.7
79	70.0	71.4	72.7	74.1	75.4	76.8	78.1	79.5	80.8	82.2
80	83.6	84.9	86.3	87.6	89.0	90.3	91.7	93.0	94.4	95.7
81	97.1	98.4	99.8	*01.2	*02.5	*03.9	*05.2	*06.6	*07.9	*09.3
82	1110.6	12.0	13.3	14.7	16.1	17.4	18.8	20.1	21.5	22.8
83	24.2	25.5	26.9	28.2	29.6	31.0	32.3	33.7	35.0	36.4
84	37.7	39.1	40.4	41.8	43.1	44.5	45.9	47.2	48.6	49.9
85	51.3	52.6	54.0	55.3	56.7	58.0	59.4	60.7	62.1	63.5
86	64.8	66.2	67.5	68.9	70.2	71.6	72.9	74.3	75.6	77.0
87	78.4	79.7	81.1	82.4	83.8	85.1	86.5	87.8	89.2	90.5
88	91.9	93.3	94.6	96.0	97.3	98.7	*00.0	*01.4	*02.7	*04.1
89	1205.4	06.8	08.2	09.5	10.9	12.2	13.6	14.9	16.3	17.6
90	19.0	20.3	21.7	23.1	24.4	25.8	27.1	28.5	29.8	31.2
91	32.5	33.9	35.2	36.6	37.9	39.3	40.7	42.0	43.4	44.7
92	46.1	47.4	48.8	50.1	51.5	52.8	54.2	55.6	56.9	58.3
93	59.6	61.0	62.3	63.7	65.0	66.4	67.7	69.1	70.5	71.8
94	73.2	74.5	75.9	77.2	78.6	79.9	81.3	82.6	84.0	85.4
95	86.7	88.1	89.4	90.8	92.1	93.5	94.8	96.2	97.5	98.9
96	1300.2	01.6	03.0	04.3	05.7	07.0	08.4	09.7	11.1	12.4
97	13.8	15.1	16.5	17.9	19.2	20.6	21.9	23.3	24.6	26.0
98	27.3	28.7	30.0	31.4	32.8	34.1	35.5	36.8	38.2	39.5
99	40.9	42.2	43.6	44.9	46.3	47.7	49.0	50.4	51.7	53.1
100	54.4	55.8	57.1	58.5	59.8	61.2	62.5	63.9	65.3	66.6
200	2708.7	10.0	11.4	12.7	14.1	15.5	16.8	18.2	19.5	20.9
300	4062.8	64.2	65.5	66.9	68.2	69.6	71.0	72.3	73.7	75.0

	1.4
0.1	0.1
0.2	0.3
0.3	0.5
0.4	0.6
0.5	0.7
0.6	0.8
0.7	1.0
0.8	1.1
0.9	1.3

If the temperature of the mercury is other than 20° a correction is applied using Table IV.

TABLE IV.—VALUES OF *N*. CORRECTION IN PRESSURES (GRAMS PER SQUARE CENTIMETER) FOR VARIOUS TEMPERATURES AND MERCURIAL HEIGHTS

Temperature, degrees Centigrade	Height of mercury, centimeters									
	10	20	30	40	50	60	70	80	90	100
5	0.4	0.7	1.1	1.5	1.8	2.2	2.6	2.9	3.3	3.7
6	0.3	0.7	1.0	1.4	1.7	2.1	2.4	2.7	3.1	3.4
7	0.3	0.6	1.0	1.3	1.6	1.9	2.2	2.6	2.9	3.2
8	0.3	0.6	0.9	1.2	1.5	1.8	2.1	2.4	2.6	2.9
9	0.3	0.5	0.8	1.1	1.4	1.6	1.9	2.2	2.4	2.7
10	0.2	0.5	0.7	1.0	1.2	1.5	1.7	2.0	2.2	2.4
11	0.2	0.4	0.7	0.9	1.1	1.3	1.5	1.8	2.0	2.2
12	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0
13	0.2	0.3	0.5	0.7	0.9	1.0	1.2	1.4	1.5	1.7
14	0.2	0.3	0.4	0.6	0.7	0.9	1.0	1.2	1.3	1.5
15	0.1	0.2	0.4	0.5	0.6	0.7	0.9	1.0	1.1	1.2
16	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
17	0.1	0.1	0.2	0.3	0.4	0.4	0.5	0.6	0.7	0.7
18	0.1	0.1	0.2	0.2	0.2	0.3	0.3	0.4	0.4	0.5
19	0.0	0.0	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.2
20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
21	0.0	0.0	−0.1	−0.1	−0.1	−0.2	−0.2	−0.2	−0.2	−0.2
22	−0.1	−0.1	−0.1	−0.2	−0.2	−0.3	−0.3	−0.4	−0.4	−0.5
23	−0.1	−0.1	−0.2	−0.3	−0.4	−0.4	−0.5	−0.6	−0.7	−0.7
24	−0.1	−0.2	−0.3	−0.4	−0.5	−0.6	−0.7	−0.8	−0.9	−1.0
25	−0.1	−0.2	−0.4	−0.5	−0.6	−0.7	−0.9	−1.0	−1.1	−1.2
26	−0.2	−0.3	−0.4	−0.6	−0.7	−0.9	−1.0	−1.2	−1.3	−1.5
27	−0.2	−0.3	−0.5	−0.7	−0.9	−1.0	−1.2	−1.4	−1.5	−1.7
28	−0.2	−0.4	−0.6	−0.8	−1.0	−1.2	−1.4	−1.6	−1.8	−2.0
29	−0.2	−0.4	−0.7	−0.9	−1.1	−1.3	−1.5	−1.8	−2.0	−2.2
30	−0.2	−0.5	−0.7	−1.0	−1.2	−1.5	−1.7	−2.0	−2.2	−2.4
31	−0.3	−0.5	−0.8	−1.1	−1.4	−1.6	−1.9	−2.2	−2.4	−2.7
32	−0.3	−0.6	−0.9	−1.2	−1.5	−1.8	−2.1	−2.4	−2.6	−2.9
33	−0.3	−0.6	−1.0	−1.3	−1.6	−1.9	−2.2	−2.6	−2.9	−3.2
34	−0.3	−0.7	−1.0	−1.4	−1.7	−2.1	−2.4	−2.7	−3.1	−3.4
35	−0.4	−0.7	−1.1	−1.5	−1.8	−2.2	−2.6	−2.9	−3.3	−3.7

The correction for the difference in level between the middle of the manometer and the viscometer is made negligible in setting up the apparatus.

MEASUREMENT OF TIME

We have seen that the pressure in grams per square centimeter must always be 30 times as great as the distance between the bulbs. On the other hand the pressure must always be kept small enough so that the time of flow can be measured to the desired accuracy. Thus the time should not fall below 200 sec. since one cannot measure the time more accurately than to 0.2 sec. with a stop-watch.

The stop-watch should be tested repeatedly against the second hand of a good time piece. It should not gain or lose as much as 0.2 sec. in 5 min. It is well to keep the watch in the same position during successive measurements, as well as not to allow it to be nearly run down during a measurement. In selecting a stop-watch it should be noted that watches show better performance whose mechanism continues to run whether the split-second hand is in use or not. The performance of the watch may be tested at the U. S. Bureau of Standards.

TEMPERATURE

The viscometer is kept at a constant temperature by means of a large, well-stirred bath which is regulated by hand, if a series of temperatures are to be measured, or by a thermostat, if the bath is to be used for a long time at a single temperature. Since at 0° the fluidity of water increases 0.1 per cent for every 0.03° rise in temperature it is clear that the temperature regulation must be to at least 0.03°. For more viscous substances a still more precise regulation is necessary if the same degree of accuracy is to be obtained.

A thermometer should be used which is graduaded to tenths and calibrated through its entire length. The ice point should be determined from time to time. If it is impracticable to have the entire thread of mercury immersed at all times a correction should be made for the emergent stem. The following table may be used:

TABLE V.—CORRECTION OF A NORMAL THERMOMETER FROM 0° TO 100°C
FOR EMERGENT STEAM GRADUATED IN TENTHS OF A DEGREE

Number of degrees of mercury exposed	Difference in temperature between mean temperature of emergent steam and bath. Corrections in degrees to be added to the observed temperature					
	30°	40°	50°	60°	70°	80°
10	0.05	0.05	0.05	0.05	0.10	0.10
20	0.10	0.15	0.15	0.15	0.20	0.20
30	0.20	0.25	0.25	0.25	0.30	0.35
40	0.30	0.30	0.35	0.40	0.45	0.50
50	0.35	0.40	0.45	0.50	0.55	0.60

Since measurements are always preferred for even degrees it is a great advantage for the worker to have on the bath before him a table showing what temperatures on the thermometer must be employed in order to obtain a desired even temperature. The temperatures of 0°, 10°, 20°, 40°, 60°, 80°, 100° are sufficient to give a good curve over this range.

THE PRESSURE REGULATOR

Viscosity measurements have usually been carried out without the use of a pressure regulator, but due to the withdrawal of the air in use and to possible small leaks in the connections and to changes in temperature, the pressure rises and falls and is hardly ever constant during the time of a single measurement. With a pressure regulator the pressure will often stay constant to the limit of the experimental error for a day or more at a time, without temperature regulation of the room, heat insulation of the apparatus or any particular care in using the air. Not only is this a saving of time and annoyance to the experimenter but by using only a few pressures at the most there is a considerable saving of time in calculation. Hence the pressure regulator is a necessity for extended work.

The diagrammatic view of the apparatus with pressure regulator is given in Fig. 92. Air is forced in through a needle valve A to a storage reservoir B whose pressure in pounds per square inch is shown on the gauge C. In adjusting the pressure regulator the air is very slowly admitted to the stabilizing reservoir F by

means of the needle valve D.   The valve E is convenient in locating leaks in the apparatus, etc., but is not often used.   The valve G is a direct connection to air which is also seldom used.

The pressure regulator consists of five brass tubes 6 cm. in diameter which are filled with water let in at K, the valves O', O'' etc. being open and the valve N closed.   When the water begins to overflow at M into the drain pipe, the water is shut off
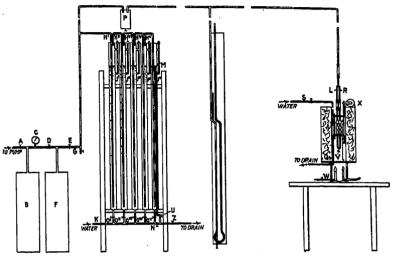
FIG. 92.—Diagram of viscometer set-up with multiple tube water stabilizer.

at K, and as soon as equilibrium is reached, the drain pipe is also closed off at Z and the valves O', O'', etc. are closed.

By allowing air to pass *very* slowly through the valve D the air will be gradually forced down the tube H' until it bubbles out through the water, and, if the pet-cock J' is open, into the air. If the stream of air is very slow, say a bubble or two per second, it is evident that the pressure will be constant.   If a higher pressure is desired the pet-cock J' is closed when the pressure becomes the sum of the pressures obtained by the two tubes separately and so on for the five different pressures up to the maximum capacity of the regulator.   In lowering the pressure one must be careful to turn the pet-cocks to air in the reverse order J^V J^{IV} J^{III} and J^{II} J^{I} in order that the air under pressure may not cause the water to be drawn back into the system.   The advan-

20

tage of the drain pipe U is that of securing day by day practically identical pressures, without the loss of time in adjustment. If other pressures than these are desired, they may be obtained by drawing off some of the water from one or more of the stand pipes. The glass gage at J', etc., aid the manipulator in adjusting the current of air. They may be cleaned by unscrewing the pet-cocks above and using a small brush.
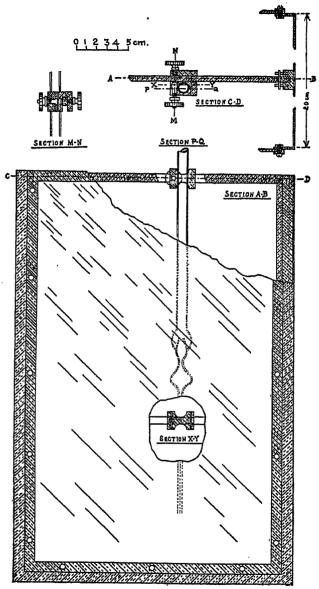
The beginner must be cautioned particularly against turning the system to air at the viscometer since it may result in filling the manometer, etc. with water. To prevent such an accident and to dry the air, the reservoir P containing granular calcium chloride is introduced. Any liquid should be drained at intervals.

THE MANOMETER

The manometer consists of a plate glass mirror which must be mounted vertically, on which is stretched a 2-m steel tape graduated in millimeters. Over the tape is fixed the glass tube of the manometer bent so that both the right and left limbs may be read on the same tape. The manometer may be filled with either mercury or water. If water is used for low pressures another manometer will be desired for mercury. Since it is possible to read the manometer to 0.01 cm one can use the mercury manometer down to 10 cm (135 g per square centimeter) with the desired accuracy. With water one can go down to about 50 g per square centimeter, but not much further unless a correction is made for the true average pressure. A thermometer near the middle of the manometer is needed to give the temperature of the manometer fluid.

THE BATH

The viscometer V is mounted on a massive brass frame Fig. 93 by means of brass clips designed especially for this purpose. The frame slides in grooves on the side of the bath so that the viscometer may be easily kept in a vertical position. The viscometer is connected by heavy-walled rubber tubing to the pressure by way of the three-way glass stop cocks L and R, the third connection being to air. The temperature of the bath is raised by means of a burner W which is connected without the use of rubber to the gas supply. The second burner Y with stop cock and pilot flame is used as needed to obtain the fine regulation.

Fig. 93.—Details of bath, frame, and clips for holding viscometer.

To assist in the regulation, cold water is admitted, when desired, by a cock at S. A drain pipe, Q, maintains the bath at a constant level. It may also be unscrewed to permit draining the water from the bath. The bath is insulated on two sides.

THE DENSITY

It is not necessary to know the exact density in order to obtain the fluidity by this method. But the density can be measured at the same time with accuracy with little additional labor. Since the fluidity is very closely related to the volume, according to the law that the fluidity is directly proportional to the free volume, the specific volume should usually be obtained with precision.

The instrument shown in Fig. 94 is convenient to use and unlike the Sprengel pycnometer, it can be used to determine the density below room temperature. It is filled to the mark with water and weighed at every temperature at which it is to be used. It is then cleaned, dried, weighed, and filled with the liquid to be determined and again weighed. The ratio of the weights of liquid corrected simply for the buoyancy of the air gives the correct specific gravity referred to water at 4°C. The densities of water are given in Table VI.

FIG. 94.—
A pycnometer
for liquids.

TABLE VI.—DENSITY AND VOLUME OF WATER IN GRAMS PER MILLILITER

Temperature	Density	Logarithm density	Specific volume
0	0.99987	9.99994 − 10	1.00013
10	0.99973	9.99988 − 10	1.00027
20	0.99823	9.99923 − 10	1.00177
30	0.99568	9.99811 − 10	1.00435
40	0.99225	9.99662 − 10	1.00782
50	0.98807	9.99479 − 10	1.01207
60	0.98324	9.99266 − 10	1.01705
70	0.97781	9.99025 − 10	1.02270
80	0.97183	9.98759 − 10	1.02899
90	0.96534	9.98468 − 10	1.03590
100	0.95838	9.98154 − 10	1.04343

The formula to be used in obtaining the density is:

$$\rho_4{}^t = \frac{w'}{w_0}\rho_0 + 0.0012\left(\frac{w' - w_0}{w_0}\right)$$

where w' = weight of liquid at $t°$C,

w_0 = weight of water at $t°$C,

ρ_0 = density of water at $t°$C.

The liquid is introduced or removed from the pycnometer by
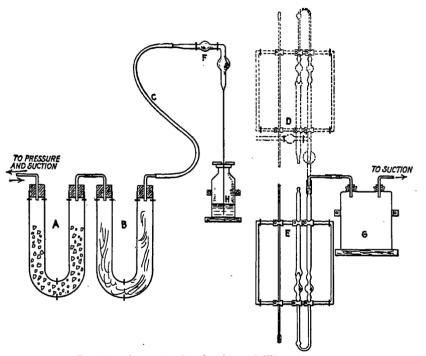
FIG. 95.—Apparatus for cleaning and filling viscometer.

means of the capillary pipette, used also for introducing liquid into the viscometer, shown in Fig. 95.

This rubber tubing as well as the heavy walled tubing at the top of the viscometer should be scrupulously cleaned on the *inside* to remove dust before they are used.

If the capillary stem of a 25 ml pycnometer has a bore of 0.08 cm it is capable of an accuracy of 0.01 per cent by reading the meniscus to within 1 mm. It is well to have two pycnometers

of equal size and employ the tare method in weighing.

Strictly, it is necessary to measure the density at only one temperature by this method. The working volume of the viscometer has to be adjusted each time that the temperature of the liquid is raised. By noting the expansion of this working volume for each temperature interval it is readily possible to calculate the specific volume and density. The portion of the viscometer HG, Fig. 29, is graduated in millimeters. By filling the viscometer with mercury from A to G, and weighing this mercury, the working volume V' can be actually determined. And by filling a given length of the capillary HG with mercury, the volume v' of the capillary per centimeter is easily determined. The density of mercury is given in Table III.

TABLE VII.—DENSITY AND VOLUME OF MERCURY IN GRAMS PER MILLILITER

Temperature, degrees	Density	Logarithm density	Specific volume
10	13.570	1.13260	0.073687
15	13.558	1.13220	0.073757
20	13.546	1.13181	0.073822
25	13.534	1.13142	0.073887
30	13.522	1.13104	0.073954

If, therefore, the specific volume of the liquid is s_0 at temperature t_o and on forcing the meniscus at the left just up to the trap, the right meniscus is a distance d away from its proper level G, then at the new temperature t, the specific volume s must be

$$s = \frac{s_0}{V'}\left(1 + v'd\right) = \frac{1}{\rho} \tag{10}$$

With this volumeter it must be remembered that the errors are cumulative. On the other hand with the pycnometer method care must be taken to wipe off drops of liquid which may adhere to the inside of the glass, and to prevent the evaporation of volatile substances, on account of which a stopper is added to the pycnometer.

Assuming that a capillary is used whose radius is 0.01 cm and that the tube HG has a radius which is ten-fold this amount, or

0.1 cm (*cf.* page 319) reading the meniscus to 0.1 mm will give an accuracy in the specific volume of 0.01 per cent.

CLEANING AND FILLING THE VISCOMETER

The viscometer is not removed from its frame during the course of an investigation. Two hooks are screwed into a board on the wall which will hold the viscometer frame firmly at *E*, Fig. 95. Chromic acid, added with pipette, is drawn through the instrument by means of suction. The frame and viscometer are then again placed on hooks in an inverted position *D* and the liquid withdrawn by means of suction. A Woulff flask is interposed between the rubber tubing and the suction line. The apparatus is washed out repeatedly with dust-free water and finally with dust-free alcohol and dust- and grease-free ether. Air which has passed over granulated calcium chloride *A* and through a long column of absorbent cotton *B* is then drawn through using clean rubber tubing.

To fill the instrument an amount of liquid slightly greater than the working volume is drawn up into the clean pipette *F* which is wiped free of dust by means of chamois skin just before use. The liquid is protected from the moisture of the air by means of the drying tube containing calcium chloride held in position by means of absorbent cotton.

THE VISCOSITY RECORD

The data may be kept on sheets ruled somewhat as follows: which will give a compact and systematic record of both data and the calculations:

TABLE VIII.—LAFAYETTE COLLEGE VISCOSITY RECORD

Page I

Substance___**Pure Water**___   Remarks___**Calibration**___

Date_____ Observer___**W. G. K.**___   = .**0.45**

Viscometer No. **5**, Pycnometer No. **2**

Log C' = **8.37598–10** Log $\dfrac{C'}{C}$ = **5.22122**

| Temperature bath | Limb | Time | | Time, seconds | Manometer, upper reading, lower reading | | Temperature | Sum difference = h_0 | Weight pyc. |
		Minutes	Seconds		Start	Finish			
20	L	5	7.0	807.0	259.46 28.12	259.46	21.2	287.58 231.34	
20	R	5	8.2	308.2	259.48 28.12	259.48	21.1	287.60 231.36	

ρ	$h_1\rho$	K	$\pm h_1$ $\rho K \pm L$	P_0	$\dfrac{C'_1\rho}{Ct^2}$	P	η in cp	φ	v	Remarks
0.9982	+.44 −.44	−.79 −.79	−.35 −1.23	230.99 230.13	1.76 1.75	229.23 228.38	1.0050 1.0052	99.50 99.48		water mano-meter

CALCULATION OF CONSTANTS

Let us use the above data for water at 20° to show the method of calculation of constants, etc.   We record the sum of the upper and lower manometer readings merely as a check against error in reading, since this sum should be constant.   With our instrument $V = 4.0$ ml, and $l = 7.5$ cm hence $C' = 0.02377$.   The value of 231.34, corrected by Table II for K gives

$$
\begin{aligned}
200 \text{ cm at } 21.2° &= 0.69 \\
30 \text{ cm at } 21.2° &= 0.10 \\
1.34 \text{ cm at } 21.2° &= \underline{0.00} \\
\text{Total correction} &= 0.79 \\
p_1 = 231.34 - 0.79 &= 230.55 \text{ cm}
\end{aligned}
$$

The value of L is negligible. Calculating the approximate value of C using Eq. (3) we have,

$$\frac{0.01005 \times 307 + 0.02377 \times 0.998}{230.55 \times 307 \times 307} = 1.431 \times 10^{-7}$$

Calculating now the hydrostatic head, using this value of C, we have from Eq. (5)

$$h_1 = 0.44 + 0.01 = 0.45.$$

Now $p = 230.55 + 0.45 = 231.0$ for the left limb or
$$= 230.57 - 0.45 = 230.1 \text{ for the right limb;}$$

hence, on applying again Eq. (3) the true value of C becomes

$$C = \frac{0.1005 \times 307 + 0.02377 \times 0.998}{231 \times 307 \times 307} = 1.428 \times 10^{-7}.$$

EXAMPLE OF CALCULATION OF VISCOSITY AND FLUIDITY

Suppose that we assume that we had given the constants of the apparatus, and that we desired to calculate out the viscosity. We have $h_1 = + 0.45$, $K = -0.79$, so that the corrected pressure is 231.0. We may now apply Eq. (1) at once, but advantages may be obtained, without extra labor, by calculating the value of P in the equation

$$Cpt - C'\rho/t = CPT$$
$$P = p - \frac{C'\rho}{Ct^2} \tag{11}$$

which is evidently the pressure consumed in overcoming viscous resistance solely. In this case $\frac{C'\rho}{Ct^2} = 1.76$ hence $P = 229.2$. The fluidity φ is

$$\varphi = \frac{1}{CPt} = \frac{1}{\eta} = 99.5 \quad \text{c.g.s. units.}$$

Instead of writing the viscosity as 0.01005 we prefer to multiply by 100 and record the datum as 1.005 centipoises (cp), which keeps most viscosities from becoming inconveniently small fractions and it also makes the viscosities "specific," referred to water at practically 20°.

In scrutinizing the data heretofore published on viscosity one is particularly interested in the magnitude of the kinetic energy correction and it may be subject to slight changes in the future.

Publication of the temperature, time, pressures p and P, density, viscosity, and fluidity makes the data quite complete and correction easy.

In constructing the viscometer, the glass blower must select a piece of capillary tubing which has not only a uniform bore but also one which has a radius which must be selected within rather narrow limits. This requires the measurement of the radius, which is accomplished as follows. The capillary is filled with mercury completely to a distance of exactly 10 cm, this mercury is then run out on to a watch crystal and weighed. The radius of the capillary in centimeters can be read at once from Table IX. These measurements need not be exact, but where it is desired to measure the average radius with exactitude, as in absolute measurement, it is to be noted that the volume of the mercury is calculated for 20°C and that the values are corrected for buoyancy of the air so that there is no correction in weighing with platinum weights. It is assumed that the mercury thread is a true cylinder.

Having found the radius of the capillary, it becomes feasible to cut off a length which will give a time of flow of not less than 200 sec. for the assumed maximum fluidity, *e.g.*, 500, with a pressure of 50 g per square centimeter and a volume of flow of 4 ml. The lengths to be cut off for capillaries of different radii are given in Table X (*cf.* also Fig. 24).

The table shows that with a maximum fluidity of 500 and a permissible length of capillary up to 20 cm, the radius must not be as great as 0.015 cm; and if the ratio of the length to the radius is to be greater than 500 in order to minimize "end effects," the radius must be over 0.010 cm, which limits the selection within quite narrow limits.

The viscometer with a 500 capillary will serve for quite viscous liquids, for the pressure can be varied from 50 to 10,000 and the time may conveniently be increased fivefold, hence one can measure two-thousand-fold, *i.e.*, from 500 to 0.5. Nevertheless in an investigation in which no fluidities are to be measured above 50, it is convenient to use a viscometer with a maximum of 50, and therefore the length of capillary will be one-tenth of that indicated by Table X. Just what maximum to specify, as 5,000 500, 50, 5, or 0.5, may easily be judged by the use of Tables XI

TABLE IX.—THE AVERAGE RADIUS OF A CAPILLARY TUBE IN CENTIMETERS CORRESPONDING TO THE WEIGHT OF MERCURY REQUIRED TO FILL A LENGTH OF 10 CM AT 20°

Radius, centimeters	Weight, grams	Difference	Radius, centimeters	Weight, grams	Difference
0.001	0.0004	12	0.051	1.1068	438
0.002	0.0016	12	0.052	1.1506	447
0.003	0.0038	30	0.053	1.1953	455
0.004	0.0068	38	0.054	1.2408	464
0.005	0.0106	47	0.055	1.2872	472
0.006	0.0153	56	0.056	1.3344	481
0.007	0.0209	63	0.057	1.3825	490
0.008	0.0272	73	0.058	1.4315	498
0.009	0.0345	81	0.059	1.4813	506
0.010	0.0426	89	0.060	1.5319	515
0.011	0.0515	98	0.061	1.5884	523
0.012	0.0613	106	0.062	1.6357	532
0.013	0.0719	115	0.063	1.6889	541
0.014	0.0834	123	0.064	1.7430	549
0.015	0.0957	132	0.065	1.7979	557
0.016	0.1089	141	0.066	1.8536	566
0.017	0.1230	149	0.067	1.9102	575
0.018	0.1379	157	0.068	1.9677	582
0.019	0.1536	166	0.069	2.0259	592
0.020	0.1702	175	0.070	2.0851	600
0.021	0.1877	183	0.071	2.1451	608
0.022	0.2060	191	0.072	2.2059	617
0.023	0.2251	200	0.073	2.2676	626
0.024	0.2451	209	0.074	2.3302	634
0.025	0.2660	217	0.075	2.3936	643
0.026	0.2877	225	0.076	2.4579	651
0.027	0.3102	234	0.077	2.5230	659
0.028	0.3336	243	0.078	2.5889	668
0.029	0.3579	251	0.079	2.6557	677
0.030	0.3830	259	0.080	2.7234	685
0.031	0.4089	268	0.081	2.7919	694
0.032	0.4357	277	0.082	2.8613	702
0.033	0.4634	285	0.083	2.9315	711
0.034	0.4919	294	0.084	3.0026	719
0.035	0.5213	302	0.085	3.0745	727
0.036	0.5515	311	0.086	3.1472	736
0.037	0.5826	319	0.087	3.2208	745
0.038	0.6145	327	0.088	3.2953	753
0.039	0.6472	336	0.089	3.3706	762
0.040	0.6808	345	0.090	3.4468	770
0.041	0.7153	353	0.091	3.5238	779
0.042	0.7506	362	0.092	3.6017	787
0.043	0.7868	370	0.093	3.6804	796
0.044	0.8238	379	0.094	3.7600	804
0.045	0.8617	387	0.095	3.8404	813
0.046	0.9004	396	0.096	3.9217	821
0.047	0.9400	404	0.097	4.0038	830
0.048	0.9804	413	0.098	4.0868	838
0.049	1.0217	421	0.099	4.1706	847
0.050	1.0638	430	0.100	4.2553	855

TABLE X.—LENGTHS OF CAPILLARY FOR DIFFERENT RADII ASSUMING A MAXIMUM FLUIDITY OF 500, A MINIMUM PRESSURE OF 50 G PER SQUARE CENTIMETER, A MINIMUM TIME OF FLOW OF 200 SEC., AND A VOLUME OF FLOW OF 4 ML. $l = \dfrac{\pi g p t}{8v}\cdot r^4 \varphi$

Radius in centimeters	Length in centimeters	Difference	Radius in centimeters	Length in centimeters	Difference
0.001	0.00048		0.051	3,254	
0.002	0.00770	....	0.052	3,517	263
0.003	0.03896	....	0.053	3,796	279
0.004	0.12315	....	0.054	4,090	294
0.005	0.3007	....	0.055	4,402	312
0.006	0.6234	....	0.056	4,731	329
0.007	1.155	....	0.057	5,080	349
0.008	1.970	0.825	0.058	5,446	366
0.009	3.156	1.186	0.059	5,830	384
0.010	4.811	1.655	0.060	6,234	404
0.011	7.043	2.232	0.061	6,668	429
0.012	9.978	2.935	0.062	7,110	447
0.013	13.74	3.96	0.063	7,577	467
0.014	18.48	4.74	0.064	8,072	495
0.015	24.35	5.87	0.065	8,587	515
0.016	31.53	7.18	0.066	9,126	539
0.017	40.18	8.65	0.067	9,693	567
0.018	50.50	10.32	0.068	10,285	592
0.019	62.68	12.18	0.069	10,904	619
0.020	76.97	14.29	0.070	11,550	646
0.021	93.56	16.60	0.071	12,224	674
0.022	112.7	19.12	0.072	12,926	702
0.023	134.6	21.94	0.073	13,662	736
0.024	159.6	25.0	0.074	14,427	765
0.025	187.9	28.3	0.075	15,221	794
0.026	219.9	32.0	0.076	16,048	827
0.027	255.7	35.6	0.077	16,909	861
0.028	295.7	40.0	0.078	17,809	900
0.029	340.3	44.6	0.079	18,737	928
0.030	389.7	48.4	0.080	19,704	967
0.031	444.3	54.6	0.081	20,708	1,004
0.032	504.4	60.1	0.082	21,750	1,042
0.033	570.3	65.9	0.083	22,830	1,080
0.034	643.0	72.7	0.084	23,950	1,120
0.035	721.8	78.8	0.085	25,111	1,161
0.036	808.0	86.2	0.086	26,314	1,203
0.037	901.8	93.8	0.087	27,560	1,246
0.038	1,003.0	101.2	0.088	28,849	1,289
0.039	1,118.0	110.0	0.089	30,182	1,333
0.040	1,232.0	119.0	0.090	31,562	1,380
0.041	1,359.0	127.0	0.091	32,988	1,426
0.042	1,497.0	138.0	0.092	34,462	1,474
0.043	1,645.0	148.0	0.093	35,985	1,523
0.044	1,803.0	158.0	0.094	37,559	1,574
0.045	1,972.0	169.0	0.095	39,183	1,624
0.046	2,154.0	182.0	0.096	40,859	1,676
0.047	2,348.0	194.0	0.097	42,587	1,728
0.048	2,554.0	206.0	0.098	44,371	1,784
0.049	2,774.0	220.0	0.099	46,210	1,839
0.050	3,007.0	233.0	0.100	48,106	1,896
		247.0			

and XII, without any preliminary measurements. Table X will then be used as already indicated.

TABLE XI.—APPROXIMATE FLUIDITIES FOR CONVENIENT REFERENCE

Substance	Fluidity
Castor oil at 20°..............................	0.1
Lard oil at 20°.................................	1.
Sugar solution at 20°, 60 per cent by weight........	1.77
Water at 20°.2................................	100.0
Aliphatic hydrocarbons and ethers at boiling temperature....................................	500.
Carbon dioxide at the critical state..............	5,000.

TABLE XII.—RADII LIMITS FOR DIFFERENT FLUIDITY MAXIMA AND l/r RATIOS

Fluidity maximum	$\dfrac{l}{r}$	Radius limits in centimeters
5,000.0	600	0.005 to 0.008
500.0	500	0.010 to 0.015
50.0	400	0.020 to 0.026
5.0	300	0.040 to 0.045
0.5	200	0.074 to 0.081

Calibrating an instrument whose maximum fluidity is below 100 offers difficulties since water at 20° is excluded. The best suggestions at present are: a 40 per cent solution by weight of ethyl alcohol in water at 0°, fluidity, 14.0; a 60 per cent sucrose solution by weight at 20°, fluidity 1.77; freshly distilled aniline at 0.5°, fluidity, 9.95.

The glass-blower should make the bulb C (and K) to have the shape of two hollow cones placed base to base, in order to secure good drainage. Bad drainage may be detected by inequality in the fluidity as determined by the right and left limbs with viscous liquids at the higher rates of flow. For very viscous liquids the time of flow must be increased so that drainage difficulties may be obviated. Increasing the size of the bulbs is no advantage.

The bulbs must be of such size that the left meniscus will not

only be at A when the right meniscus is at G, but it should be at B when the right meniscus is at J, and at D when the right meniscus is at L.

The ends of the capillary at E and F must not be contracted in under any circumstances, and as far as practicable the ends should not be expanded into a trumpet shaped opening, as this may seriously affect the kinetic energy correction. The appropriateness of the correction already given may be tested for each instrument by using a given liquid at a variety of pressures.

If the liquid is to move past the marks B and D with a velocity of not less than 0.1 cm per second when the time of flow is 200 seconds, it is only necessary to use tubing for that part of the instrument whose radius is not more than 0.25 cm. On the other hand, for absolute measurements, the instrument should always be so designed that the resistance to flow outside of the capillary will be negligible. This is ascertained as follows: Let the lengths of the tubes B, D, L, and J, Fig. 1, be in all L and their radius be R. Then R^4/L must be greater than 1,000 r^4/l. For a capillary whose radius is 0.012 cm, R must be at least 0.07 cm if $L = 1$. This value is larger than is commonly supposed. A rule which is simple but will cover every case is to have R at least 10 times the radius of the capillary.

APPENDIX B

PRACTICAL PLASTOMETRY

The measurement of the flow of plastic substances resembles that of viscous substances in most respects, but since plastic substances do not drain like liquids, it is convenient to measure the volume (or weight) of substance extruded. For this purpose the plastometer, shown in Fig. 30, p. 77, has been designed to replace the viscometer. It consists of a top A, container B, and base C with capillary D and receiver E. The top consists of a square plate of brass, through which the pressure is admitted by means of a copper tube F, which is enlarged at the end to make it convenient to connect with the pressure. The rubber gaskets H and J enable one to make the apparatus gastight, when the thumb-screws are screwed down. A brass pin K, brazed into the top, passes through the rubber gasket and into a hole in the body of the container. On the opposite side of the container, a small copper tube passes through the top, through the rubber gasket, and into a hole which extends all of the length of the container, and into the lower end of which a short piece of hollow copper tubing is affixed. This tube in turn passes through the second rubber gasket J leading into the base C, thus affording a connection between the atmosphere and the receiver while the plastometer is immersed in the bath.

The receiver is made of glass and with a flat bottom so that it will sit upright. It is held in position by means of the rubber collar M. The rod G is attached to the container in order that the plastometer may be supported by the frame shown in Fig. 89.

Through the base, there extends the capillary tube D, whose ends have been ground off flat and whose dimensions are known. To cement the capillary in position it is cleaned carefully with chromic acid mixture and dried without touching the part to be soldered. It is "tinned over" in the usual manner and soldered in place, the space N being filled with the alloy. Two parts bismuth, two parts lead and one part tin has been found satis-

factory. A more certain method is to platinize the glass and then solder in position with pure tin as solder.

To determine the effect upon the flow of changing the length and radius of the capillary, at least four capillaries may be required, hence it is convenient to keep all of them mounted continuously in duplicate bases.

Since the mercury thread gives only the radius of a cylinder which would have the same volume as the capillary, the true average radius for flow purposes requires more elaborate estimation if absolute measurements of flow are to be made and any considerable accuracy is desired. In fact, since the flow varies as the fourth power of the radius and it is measurable to the desired accuracy only with difficulty, it may be said that this is the most difficult part of absolute measurement.

Whereas one will seek to obtain a capillary tube which is a true cylinder, it will usually be slightly elliptical. In this case the ratio of the major to the minor axes may be obtained by measurements of the photomicrograph of the ends, although several other methods may be used. From this ratio and the average radius obtained by means of the mercury calibration, the actual values of the major and minor axes $2B$ and $2C$ may be calculated.[1] It follows then that

$$r^4 = \frac{2B^3C^3}{B^2 + C^2}.$$

If the capillary is a frustrum of a true cone,

$$r^4 = \frac{3R_1^3R_2^3}{R_1^2 + R_1R_2 + R_2^2}$$

where R_3 and R_2 are the radii of the two ends. If the capillary is not only conical but elliptical at the same time,

$$r^4 = \frac{3R_3^3R_4^3}{R_3^2 + R_3R_4 + R_4^2} \cdot \frac{(1 - e^2)^3}{1 + e^2}$$

where R_3 and R_4 are the average radii of the two ends, $e = \dfrac{B - C}{B + C}$, and $2B$ and $2C$ are the mean major and minor axes.

The Measurement of Plasticity

Until the pressure is admitted the flow by seepage will ordi-

[1] *Cf.* RÜCKER, *Phil. Trans.* **185A**, 438 (1894) and KNIBBS, *J. and Proc. Roy. Soc. New South Wales* **29**, 77 (1895); **30**, 186 (1896).

narily be extremely slow. It is possible therefore to wipe off the end of the capillary, put the weighed container in place, admit the pressure for a known interval of time, touch off into the container any material still adhering to the capillary and weigh. From the weight of material, the volume of flow may be calculated from the density when desired.

There is however, another convenient method which can be used when the material comes from the capillary in drops. The observer turns on the pressure and simply takes the time of formation of a convenient number of drops, making no weighing at all. Other measurements are made at the same or other pressures. Finally without cleaning off the end of the capillary a certain number of drops are counted off into a weighed receiver at the minimum pressure used and also at the maximum pressure used. From the weight of a drop at these two pressures, one can calculate the weight of a drop at any intermediate pressure provided the weight is a linear function of the pressure. By this method a large number of measurements on a given material can be completed in a single day with an accuracy of 0.3 per cent. According to measurements by H. D. Bruce the weight of the drop is not always uniform at a given pressure.

The pressure p_1 delivered to the plastometer is calculated in the manner already described (page 299 *et seq.*), correcting for the temperature of the liquid in the manometer. The plastic material exerts a hydrostatic head which must be corrected for as follows.

The initial head in the container, h, may be measured by the use of a straight, slender wire. To this is added the length of the capillary, l, hence the pressure $(h + l)\rho$ added to p_1, gives the corrected pressure p to be used in calculating the plasticity. The change of hydrostatic head in subsequent determinations may be ascertained by noting the volume of plastic material which has accumulated in the graduated receiver. In this case it is also necessary to know how much the level of the material in the container is lowered by the loss of 1 ml. A much better plan is to have a graduated glass tube of just the size to fit into the container, and open at both ends, cemented into the container. Having cut away portions of the metal of the container, the level of the material within may be read directly.

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In the measurements of plasticity it has been found that high pressures give data which may be handled more simply than the data at low pressures. But a multiple-tube stabilizer to give two atmospheres of pressure is both complicated and expensive, hence a mercury stabilizer seems desirable. However a mercury stabilizer was not used at first because as soon as the pressure became great enough to bubble through the mercury at all, a large amount of gas suddenly came off causing a violent fluctuation in the pressure. This intermittent flow of air is partly due to the failure of the mercury to wet the tube allowing a continuous air channel to be formed over a considerable distance between the mercury and the tube. This difficulty can be overcome by the amalgamation of the tube by means of sodium amalgam. A further difficulty arose from the necessity of keeping the volume of gas bubbling through the stabilizer as small as possible while maintaining the flow continuously. This trouble was completely overcome by placing a Davis-Bourneville reducing valve at the point C of the apparatus shown in Fig. 92, a flow indicator just between the needle-valve D and the pressure-reservoir F, and another flow indicator between the valve E and the mercury stabilizer.

The flow indicator consists of two similar vials connected by an inverted U-tube leading to the bottom of both vials through two-hole rubber stoppers. A little glycerol is added to one of the vials at the start and the rate of bubbling of the gas through the liquid serves to indicate the direction of movement of the gas as well as its velocity.

The mercury stabilizer consists of an single iron tube of some 25 mm internal diameter into which leads the inner tube having a diameter of 5 mm just as in the water stabilizer. The outer tube is closed at the bottom by means of a cap but near the bottom a side tube leads off for the attachment of a stout rubber tube which is connected in turn with a glass receiver of about 2 liters capacity. This receiver can be raised and lowered and hung on stout hooks provided for the purpose at frequent vertical intervals. In order to change from one pressure to another, it is necessary for mercury to be added to or taken from the stabilizer. This is very easily accomplished by simply raising or lowering the receiver. For a pressure of two atmospheres not over 10 kg

of mercury are required. Were a smaller tube used for the outer tube of the stabilizer, less mercury would be required but the manipulation might be less convenient. A photograph of the plastometer occording to the latest design used by Mr. H. D. Bruce is reproduced in the frontispiece.

TREATMENT OF PLASTICITY DATA

The data may be analyzed either algebraically or graphically. The formula for plastic flow through a capillary tube is

$$\frac{1}{\mu} = \frac{\pi R^3 t}{4}(F - f) - \frac{m\rho V}{8\pi t l} \tag{12}$$

where μ is the mobility, and f the friction or yield value. The shearing force, $F = \frac{RPg}{2l}$, is expressed in dynes per square centimeter and the pressure P is expressed in grams per square centimeter. Since the kinetic energy is generally negligible this becomes

$$\mu = \frac{Kv}{F - f} \tag{13}$$

where v is the volume of flow per second and K is a constant whose value is 384.8 $\frac{R^4}{l}$. If we substitute in Eq. (13) the values F_1, v_1 and F_2, v_2 from two observations of the flow, we find that

$$f = \frac{F_1 v_2 - F_2 v_1}{v_2 - v_1} \tag{14}$$

so that both μ and f are readily determined. Since however the weight of flow $w = v\rho$, a more convenient expression for the friction is

$$f = \frac{F_1 w_2 - F_2 w_1}{w_2 - w_1} \tag{15}$$

The friction must have a positive value for all plastic substances and the value should be constant for a given capillary so long as seepage, slipping, *et cet.*, do not intervene.

In the early stages of the development of the subject, the graphical method of treatment is desirable from many points of view. Plotting the weight of flow in grams per second as ordinates and the shear in dynes per square centimeter as abscissas, the value of the intercept of the extrapolated curve gives the value of the friction and the slope of the curve determines the mobility. The curvature indicates to what degree seepage, *et cet.*, enter in.

APPENDIX C

TECHNICAL VISCOMETERS

Instruments very different from those employed in scientific work are much in vogue both in this country and abroad for industrial purposes, particularly in the oil industry. Thus we have the Engler Viskosimeter in Germany, the Redwood Viscometer in Great Britian, the Saybolt Viscosimeter in the United States, the Barbey Ixometre in France and a host of others. Most of them seem to have been devised with the idea in mind that the time of flow of a given quantity of various liquids through an opening is approximately proportional to the viscosity, without much regard to the character of the opening. There is usually a container which is filled to a certain level and a short efflux tube opening into the air. The number of seconds required for a given quantity of liquid to flow out under gravity is taken as an indication of the viscosity.

As it was gradually realized that these times of flow were not even proportional to the true viscosities, efforts have not been wanting to reduce the times of flow to true viscosities. Since the pressure is due to an average head of liquid h, the pressure is $hg\rho$ and the viscosity formula 1, p. 295, may be written

$$\frac{\eta}{\rho} = At - \frac{B}{t}$$

Having obtained the values of the constants A and B by calibrating the viscometer with liquids of known viscosity it appears possible to calculate the kinematic viscosity η/ρ; but if absolute viscosities are desired it is necessary to make a supplementary determination of the density ρ. Thus elaborate tables and charts have been devised for converting Engler "Degrees" (cf. Ubbelohde (1907)), and Redwood (cf. Higgins (1913), Herschel (1918) or Saybolt "Seconds") into true viscosities.

The widespread use of the Saybolt viscometer in this country makes desirable the inclusion here of the specifications for its use adopted by the American Society for Testing Materials.

"1. **Viscosity.**—Viscosity shall be determined by means of the Saybolt Standard Universal Viscosimeter.

"2. **Apparatus.**—(*a*) The Saybolt Standard Universal Viscos-

Sectional View
of
Standard Oil Tube.

A	Oil Tube Thermometer.
B	Bath Thermometer.
C	Electric Heater.
D	Turntable Cover.
E	Overflow Cup.
F	Turntable Handles.
G	Steam Inlet or Outlet.
H	Steam U-Tube.
J	Standard Oil Tube.
K	Stirring Paddles.
L	Bath Vessel.
M	Electric Heater Receptacle.
N	Outlet Cork Stopper.
P	Gas Burner.
Q	Strainer.
R	Receiving Flask.
S	Base Block.
T	Tube Cleaning Plunger.
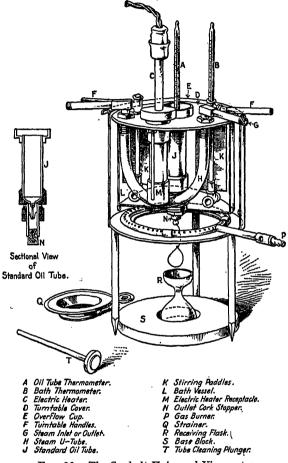
FIG. 96.—The Saybolt Universal Viscometer.

imeter (see Fig. 96) is made entirely of metal. The standard oil tube *J* is fitted at the top with an overflow cup *E*, and the tube is surrounded by a bath *L*. At the bottom of the standard oil tube is a small outlet tube through which the oil to be tested flows into a receiving flask *R*, whose capacity to a mark on its neck is

60 (±0.15) cc. The lower end of the outlet tube is enclosed by a larger tube, which when stoppered by a cork N, acts as a closed air chamber and prevents the flow of oil through the outlet tube until the cork is removed and the test started. A looped string is attached to the lower end of the cork as an aid to its rapid removal. The bath is provided with two stirring paddles K and operated by two turn-table handles F. The temperatures in the standard oil tube and in the bath are shown by thermometers, A and B. The bath may be heated by a gas ring burner P, steam U-tube H, or electric heater C. The standard oil tube is cleaned by means of a tube cleaning plunger T, and all oil entering the standard oil tube shall be strained through a 30-mesh brass wire strainer Q. A stop watch is used for taking the time of flow of the oil and a pipette, fitted with a rubber suction bulb, is used for draining the overflow cup of the standard oil tube.

"(b) The standard oil tube J should be standardized by the U. S. Bureau of Standards, Washington, D. C., and shall conform to the following dimensions:

Dimensions	Minimum, centimeters	Normal, centimeters	Maximum, centimeters
Inside diameter of outlet tube...	0.1750	0.1765	0.1780
Length of outlet tube..........	1.215	1.225	1.235
Height of overflow rim above bottom of outlet tube.........	12.40	12.50	12.60
Diameter of container of standard oil tube.................	2.955	2.975	2.995
Outer diameter of outlet tube at lower end....................	0.28	0.30	0.32

"3. **Method.**—Viscosity shall be determined at 100°F (37.8°C), 130°F (54.4°C), or 210°F (98.9°C). The bath shall be held constant within 0.25°F (0.14°C) at such a temperature as will maintain the desired temperature in the standard oil tube. For viscosity determinations at 100 and 130°F, oil or water may be used as the bath liquid. For viscosity determinations at 210°F, oil shall be used as the bath liquid. The oil for the bath liquid should be a pale engine oil of at least 350°F flash-point (open

cup). Viscosity determinations shall be made in a room free from draughts, and from rapid changes in temperature. All oil introduced into the standard oil tube, either for cleaning or for test, shall first be passed through the strainer.

"To make the test, heat the oil to the necessary temperature and clean out the standard oil tube with the plunger, using some of the oil to be tested. Place the cork stopper into the lower end of the air chamber at the bottom of the standard oil tube. The stopper should be sufficiently inserted to prevent the escape of air, but should not touch the small outlet tube of the standard oil tube. Heat the oil to be tested, outside the viscometer, to slightly below the temperature at which the viscosity is to be determined and pour it into the standard oil tube until it ceases to overflow into the overflow cup. By means of the oil tube thermometer keep the oil in the standard oil tube well stirred and also stir well the oil in the bath. It is extremely important that the temperature of the oil in the oil bath be maintained constant during the entire time consumed in making the test. When the temperature of the oil in the bath and in the standard oil tube are constant and the oil in the standard tube is at the desired temperature, withdraw the oil tube thermometer; quickly remove the surplus oil from the overflow cup by means of a pipette so that the level of the oil in the overflow cup is below the level of the oil in the tube proper; place the 60-ml flask in position so that the oil from the outlet tube will flow into the flask without making bubbles; snap the cork from its position, and at the same instant start the stop watch. Stir the liquid in the bath during the run and carefully maintain it at the previously determined proper temperature. Stop the watch when the bottom of the meniscus of the oil reaches the mark on the neck of the receiving flask.

"The time in seconds for the delivery of 60 ml of oil is the Saybolt viscosity of the oil at the temperature at which the test was made."

There is little to recommend any one of these instruments except their wide use in their respective countries. They are inaccurate and in the case of viscous oils time-consuming. With volatile solvents they cannot be used at all due to evaporation. The greatest source of error in the technical instruments is due to poor temperature control. The bath around the container is

small, the stirring ineffective and the end of the efflux tube is exposed to the air. In making duplicate determinations the liquid flows out into the air and generally cools off, so the bath is raised to somewhat above the desired temperature in order to bring the temperature back again to the large mass of oil in the container. If the run is started when the temperature comes to the proper point, it is almost impossible to prevent it going up during the run.

Another important source of error arises from the very extraordinary kinetic energy corrections encountered. The Engler instrument, for example, is normally calibrated with water at 20°C and the kinetic energy correction amounts to over 90 per cent of the total energy expended. The viscosity in this case has but little part in determining the rate of flow, and we have already seen that the coefficient (m) of the kinetic energy correction is subject to some uncertainty.

Closely connected with the kinetic energy correction, are the difficulties due to end effects and possible turbulence which are aggravated in short, wide tubes.

It is difficult to adequately clean this type of instrument or to tell when it has been properly cleaned. The liquids readily absorb dust, moisture and other impurities from the air and they may thus undergo loss or chemical change. Meissner (1910) has made a study of these sources of error. Effects of surface tension at the end of the capillary, of the changing level of liquid in the container, of slow drainage of oil down the side of the receiving flask are found to be small sources of error. With the Saybolt instrument, the flow is started by pulling out a stopper from the hollow cylinder below the efflux tube. One must see that no liquid accumulates in the air space above the stopper.

Instruments embodying the principles worked out by Coulomb and Couette have been devised by Doolittle, Stormer, and MacMichael. In the Stormer instrument a cylinder is rotated by the force arising from a falling weight, suspended by a cord carried over a pulley. The speed varies with the viscosity of the liquid and the revolutions per minute are counted. A better plan is the one adopted by MacMichael of using a constant speed, imparted to an outside cup and measuring the angle of torque produced in a disk supported in the liquid by means of a steel wire. The

instrument has considerable range, for wires of differing diameters can be used for widely differing viscosities. The readings are instantaneous and the instrument is compact and easily manipulated. The most troublesome feature of this type of instrument is the lack of constancy in the supporting wire. It is necessary to use these wires with considerable care and to calibrate frequently. Since the corrections of the instrument are not fully understood, the calibrating fluid should have nearly the same viscosity as the viscosity to be measured (*cf.* Herschel (1920)).

For liquids of high viscosity, the falling sphere method is used industrially. If the containing vessel does not have a diameter at least 10 times that of the ball, a correction must be applied Sheppard (1917). The method is admirably adapted for absolute measurements, but usually workers have felt dependent upon calibrating liquids, but since there is a dearth of calibrating fluids of high viscosity liquids are often used in which the velocity of fall is too great for the strict application of Stokes' law and a correction has to be made. Reproducible liquids of high viscosity which have been accurately determined should be available for the industrial requirements.

APPENDIX D

The measurements of Poiseuille, being somewhat inaccessible but of great practical as well as historical interest are given in detail in the following tables. Comparative values of the viscosity of water by various observers with all of the known corrections made are given in Table II. Since specific viscosities are often used, relative to water at different temperatures, we give the viscosity for water for every degree from 0 to 100 in Table III, and in Tables IV and V we give the fluidities of alcohol-water solutions and sucrose-water solutions as possible calibration fluids where water would be too fluid. For changing viscosities to fluidities the table of reciprocals (Table VI) is very convenient. To get the reciprocal of a number such as 1.007, the first part of the table is not very convenient on account of the large differences used in enterpolation. If however one uses instead 10×0.10070 in the latter part of the table, fifth column, p. 343, the number 9.93×10^{-1} is found as the reciprocal without enterpolation. The part of the table from 10.0 to 15.0 may also be used for this same purpose, in which case the reciprocal of 10.07 is found in the ninth column.

A table of four-place logarithms (Table VII) are included, and are often sufficiently exact, since viscosities are generally not more accurate than one part in 1,000.

TABLE I.—MEASUREMENTS OF POISEUILLE

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
$A°$	10.05	0.1415	0.1395	0.1430	0.1405	10	13.34085	385.870	3,505.75
								739.114	1,830.75
								773.448	1,750.00
Do.	Do.	Do.	Do.	Do.	Do.	0.6		774.291	2,327.75
						5.0		773.400	2,025.25
						10.0		773.443	1,750.00
						15.0		773.597	1,528.00
						20.0		775.093	1,344.50
						25.0		774.886	1,195.00
						30.1		775.058	1,067.50
						35.1		774.451	962.25
						40.1		774.354	871.50
						45.0		774.827	793.25
A^I	7.58	0.01420	0.01400	Do.	Do.	$10°$	Do.	51.068	20,085.0
								97.764	10,361.0
								147.834	6,851.0
								193.632	5,233.0
								387.675	2,612.5
								738.715	1,372.5
								774.676	1,308.0
A^{II}	5.11	0.01425	0.01405	Do.	Do.	Do.	Do.	98.404	6,921.0
								148.320	4,594.0
								193.421	3,515.0
								387.445	1,757.0
								774.810	878.0
A^{III}	2.555	0.01430	0.01405	Do.	Do.	Do.	Do.	387.520	880.0
								774.895	448.0
A^{IV}	1.575	Do.	Do.	Do.	Do.	Do.	Do.	24.661	8,646.0
								49.591	4,355.0
								98.233	2,194.0
								148.233	1,455.0
								194.257	1,116.0
								388.000	571.0
								775.160	298.0
A^V	0.955	Do.	Do.	Do.	Do.	Do.	Do.	23.638	5,570.0
								49.185	2,699.0
								99.221	1,360.0
								148.623	918.5
								193.315	718.0
								387.737	381.0
								774.620	207.0

TABLE I.—(*Continued*)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
A^{VI}	0.6775	Do.	Do.	Do.	Do.	Do.	Do.	24.753	3,828.75
								50.001	1,923.75
								99.343	994.00
								148.618	682.00
								193.010	537.75
								387.887	291.50
								773.790	165.75
A^{VII}	0.1?	Do.	Do.	Do	Do.	Do	Do.	4.783	3,926.75
								6.204	3,072.00
								12.129	1,685.50
								24.003	974.25
								49.040	571.75
								98.832	348.75
								148.475	267.00
								193.501	224.00
								387.972	144.00
								773.717	95.00
B	10.005	0.01135	0.01117	0.01145	0.01125	10°	8.4482	388.256	4,103.5
								739.333	2,156.0
								777.863	2,060.0
B^I	7.505	0.01140	0.01120	Do.	Do.	Do.	Do.	55.286	21,430.0
								97.922	12,079.0
								148.275	7,981.5
								193.947	6,100.0
								387.695	3,052.0
								739.467	1,600.0
								774.891	1,526.5
B^{II}	4.9875	0.01142	0.01122	Do.	Do.	Do.	Do.	99.163	7,804.0
								149.679	5,165.0
								193.441	3,997.0
								387.130	1,995.0
								774.796	999.0
B^{III}	2.3575	0.01143	0.01123	Do.	Do.	Do.	Do.	49.091	7,471.0
								98.315	3,729.0
								148.571	2,473.0
								193.877	1,892.0
								388.100	946.0
								774.880	473.0

TABLE I.—(*Continued*)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
B^{IV}	0.9000	0.01144	0.01124	Do.	Do.	Do.	Do.	24.756 49.857 99.214 149.082 193.194 387.024 774.540	5,543.0 2,762.0 1,400.0 935.0 728.9 375.0 199.0
B^{V}	0.39	0.01145	0.01125	Do.	Do.	Do.	Do.	24.290 49.578 99.139 149.098 193.130 387.024 773.282	2,386.0 1,193.0 621.0 428.0 34.00 189.0 110.0
C	10.0325		Mean diam. at 10°C 0.0085			0.5 5.0 6.0 10.0 15.2 20.0 25.1 30.1 35.1 40.1 45.1	2.1057	774.048 774.047 773.848 774.030 774.070 774.110 774.841 774.503 774.574 774.676 774.678	2,816.75 2,422.75 2,350.50 2,093.50 1,826.00 1,612.75 1,427.50 1,280.50 1,149.50 1,042.50 949.00
C	10.0325	0.00845	0.00845	0.00860	0.00850	10°	2.1057	385.158 738.969 774.030	4,210.00 2,192.00 2,093.50
C^{I}	7.495	0.00850	Do.	Do.	Do.	Do.	Do.	52.257 98.411 149.241 193.314 387.562 738.767 774.757	23,135.00 12,280.00 8,098.00 6,250.00 3,118.00 1,636.00 1,560.50
C^{II}	4.97	0.0085	0.0084	Do.	Do.	Do.	Do.	99.868 149.034 193.867 386.915 774.563	7,997.00 5,362.00 4,117.00 2,065.00 1,029.00

TABLE I.—(Continued)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
C^{III}	2.44	0.0086	0.0085	Do.	Do.	Do.	Do.	49.702	7,765.00
								98.921	3,899.00
								148.303	2,598.50
								193.544	1,994.00
								387.157	995.00
								774.677	498.00
C^{IV}	1.015	Do.	Do.	Do.	Do.	Do.	Do.	24.791	6,186.75
								49.931	3,073.00
								98.322	1,559.75
								148.795	1,029.50
								194.102	788.00
								387.191	399.00
								774.607	203.00
C^{V}	0.6025	Do.	Do.	Do.	Do.	Do.	Do.	24.192	3,587.00
								50.506	1,768.00
								99.102	904.00
								149.119	606.50
								194.217	470.00
								387.237	245.00
								773.327	131.50
D	10.080	0.004600	0.004466	0.004450	0.004250	10°	0.3629	386.247	9,708.00
								738.137	5,080.00
								773.970	4,846.00
D^{I}	5.0225	0.00454	0.00438	0.004450	0.004250	10°	Do.	54.785	35,460.00
								55.796	34,798.00
								99.508	19,517.00
								149.219	13,021.00
								192.907	10,071.00
								386.555	5,025.00
								774.617	2,506.00
Do.	Do.	Do.	Do.	Do.	Do.	5.00	Do.	774.887	2,898.50
						10.00		774.617	2,506.00
						15.00		773.271	2,199.00
						20.00		774.119	1,928.00
			Mean	diam.		25.05		775.045	1,713.75
			0.004	40406		30.07		774.356	1,532.50
						35.00		675.429	1,375.50
						40.00		774.475	1,246.75
						45.10		774.077	1,188.00

TABLE I.—(*Continued*)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
D^{II}	2.5175	0.00450	0.00430	Do.	Do.	10°	Do.	98.917	10,149.00
								147.857	6,789.00
								193.485	5,178.00
								386.847	2,589.50
								773.985	1,293.00
D^{III}	0.995	0.004466	0.004286	Do.	Do.	Do.	Do.	50.374	7,978.00
								97.124	4,136.00
								148.248	2,706.00
								192.707	2,084.75
								387.419	1,038.00
								775.866	519.00
D^{IV}	0.335	0.00445	0.00425	Do.	Do.	Do.	Do.	23.884	5,479.00
								50.276	2,611.75
								97.440	1,373.00
								147.889	897.50
								193.459	697.00
								387.062	349.00
								772.117	176.00
E	2.31	0.00286	0.00286	0.003000	0.002933	10°	0.125	58.211	26,625.00
								386.218	4,020.00
								737.829	2,103.00
								774.017	2,006.00
			Mean diam. 0.002938			0.50		773.808	2,705.00
						5.00		774.757	2,318.50
						10.00		774.017	2,006.00
						15.00		773.709	1,756.75
						20.00		773.475	1,547.25
E	Do.	Do.	Do.	Do.	Do.	25.10	Do.	774.081	1,372.25
						30.05		775.271	1,227.25
						35.07		774.563	1,102.50
						40.10		775.329	997.75
						45.00		774.635	908.75
E^{I}	0.85	0.003000	0.002933	Do.	Do.	10°	Do.	96.693	5,903.50
								147.588	3,868.00
								193.100	2,955.00
								386.787	1,469.00
								773.880	736.75
E^{II}	0.210	Do.	Do	Do.	Do.	Do.	Do.	24.301	5,651.00
								49.994	2,751.00
								96.123	1,426.00
								148.307	925.00
								193.357	707.00
								386.852	354.00
								773.223	178.00

TABLE I.—(*Continued*)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
F	38.3825	0.06932	0.06160	0.06900	0.06140	10°	17.566	126.92	1,623.00
								303.08	678.00
								667.42	306.00
								1,352.10	150.00
								1,981.50	104.00
								2,620.34	78.00
								5,198.60	40.25
								10,462.08	20.00
F_I	20.000	0.06900	0.06140	0.06932	0.06160	10°	Do.	83.36	.1,295.00
								127.60	838.00
								163.71	657.00
								328.82	326.00
								661.29	162.00
								1,321.87	81.50
								1,981.76	56.00
								2,626.58	42.00
								5,210.27	22.50
								10,459.10	12.50
F_II	9.9725	Do	Do	Do.	Do.	Do.	Do.	81.83	666.00
								163.97	328.00
								331.51	165.00
								664.36	84.50
								1,323.58	45.00
								1,984.95	31.00
								2,585.33	25.00
								5,207.73	15.00
								10,454.54	9.00
F_III	5.045	0.06910	0.06150	Do.	Do.	Do.	Do.	82.08	345.00
								163.78	175.00
								329.77	91.00
								660.97	50.00
								1,323.56	28.00
								1,983.20	21.75
								2,590.76	17.50
								5,160.07	11.00
								10,456.45	7.00
F_IV	2.600	0.06932	0.06160	Do.	Do.	Do.	Do.	82.36	191.00
								163.39	104.00
								328.04	59.75
								661.59	35.00
								1,321.19	21.75
								1,985.00	16.75
								2,614.60	13.50
								5,205.08	9.00
								10,458.02	6.00

TABLE I.—(*Continued*)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
F^V	1.075	Do.	Do.	Do.	Do.	Do.	Do.	74.29 83.89 162.89 329.39 653.49 1,306.69 1,985.29 2,606.37 5,146.62 10,456.65	114.00 130.00 63.00 39.00 25.00 16.00 13.00 10.75 7.50 5.00
G	96.200	0.06660	0.06000	0.06932	0.06180	8.60 8.70 8.80	17.566	1,087.200 1,586.340 2,084.060 2,602.300	407.00 281.00 213.00 170.00
G^I	80.000?	Do.	Do.	Do.	Do.	18.70 18.90 18.90 18.90 18.80 18.70 18.80 18.80	Do.	145.300 269.220 520.240 1,019.870 2,014.160 3,437.860 6,841.370 10,191.540	2,290.00 1,232.00 634.00 323.00 162.00 97.00 48.75 33.00
G^{II}	40.000	0.06932	0.06180	0.069321?	0.06160?	18.95 19.25 19.30 19.50 19.50	Do.	145.300 269.220 518.940 1,019.670 2,014.360	1,115.00 597.00 305.50 155.00 79.75
H	6.600	0.00133	0.00133			11.00 11.00 11.10	0.5	2,316.870 3,837.000 6,117.600	9,048.00 5,438.00 3,460.00
I	25.800	0.010	0.008			10.80 10.90 11.00 11.00 7.50	1.0	3,850.160 4,610.230 5,370.130 6,127.360 6,130.080	388.00 319.00 267.00 235.00 261.00
K	36.400	0.01316	0.01316			11.00 11.00 11.00 11.00 12.00	1.0	54.987 210.129 419.645 835.555 1,576.000	8,590.00 2,250.00 1,125.75 565.00 286.00

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TABLE I.—(Continued)

Designation of tube	Length in centimeters	Diameter of capillary in centimeters				Temperature of experiment	Volume of bulb in cc at 10°C	Pressure in millimeters mercury at 10°C	Time of efflux of volume of bulb in seconds
		Open end		Bulb end					
		Major axis	Minor axis	Major axis	Minor axis				
K	36.400	0.01316	0.01316			11.00 11.00 11.00 11.00 11.00 11.00 7.00	1.0	2,338.376 3,095.540 3,856.939 4,616.534 5,376.534 6,136.534 6,136.534	197.50 154.00 123.00 106.25 88.25 77.50 86.75
M	1.850	0.00140	0.00139	0.00140	0.00139	10.00	0.0049089	775.000	1,240.00
M¹	0.125	Do.	Do.	Do.	Do.	Do.	Do.	775.000	84.50

TABLE II.—VISCOSITY OF WATER IN CENTIPOISES AS DETERMINED BY DIFFERENT OBSERVERS

Tempera-ture	Poiseuille				Sprung	Slotte	Thorpe and Rodger	Hosking	Bing-ham and White	Average	Calcu-lated by formula
	A°	C	D'	E							
0	1.7755	1.7900	.....	1.7944	1.777	1.807	1.7766	1.7928	1.7960	1.7887	1.7921
5	1.5108	1.5137	1.5143	1.5142	1.5089	1.523	1.5083	1.522	1.5241	1.5155	1.5188
10	1.3045	1.3078	1.3088	1.3088	1.2995	1.313	1.3014	1.3105	1.3002	1.3061	1.3077
15	1.1385	1.1464	1.1465	1.1456	1.1334	1.143	1.1324	1.142	1.1373	1.1406	1.1404
20	1.0028	1.0073	1.0063	1.0087	0.9978	1.007	1.0005	1.006	1.0054	1.0046	1.0050
25	0.8900	0.8964	0.8966	0.8973	0.8947	0.895	0.8900	0.8926	0.8940	0.8941	0.8937
30	0.7958	0.8016	0.8011	0.8027	0.8183	0.802	0.7965	0.800	0.7991	0.8019	0.8007
35	0.7154	0.7194	0.7190	0.7207	0.7216	0.723	0.7190	0.724	0.7223	0.7205	0.7225
40	0.6466	0.6523	0.6508	0.6531	0.6558	0.656	0.6525	0.657	0.6557	0.6533	0.6560
45	0.5867	0.5934	0.5937	0.5932	0.6001	0.601	0.5959	0.600	0.5984	0.5958	0.5988
50	.....	.....	.....	.....	0.5512	0.552	0.5464	0.5500	0.5491	0.5497	0.5494
55	.....	.....	.....	.....	.....	0.509	0.5044	0.508	0.5073	0.5072	0.5064
60	.....	.....	.....	.....	.....	0.471	0.4676	0.469	0.4728	0.4701	0.4688
65	.....	.....	.....	.....	.....	0.437	0.4343	0.436	0.4362	0.4359	0.4355
70	.....	.....	.....	.....	.....	0.407	0.4048	0.406	0.4069	0.4062	0.4061
75	.....	.....	.....	.....	.....	0.380	0.3782	0.380	0.3794	0.3794	0.3799
80	.....	.....	.....	.....	.....	0.356	0.3547	0.356	0.3558	0.3556	0.3565
85	.....	.....	.....	.....	.....	0.334	0.3336	0.335	0.3337	0.3341	0.3355
90	.....	.....	.....	.....	.....	0.315	0.3140	0.316	0.3133	0.3146	0.3165
95	.....	.....	.....	.....	.....	0.297	0.2970	0.300	0.2983	0.2981	0.2994
100	.....	.....	.....	.....	.....	0.281	0.2814	0.284	.....	0.2821	0.2838

TABLE III.—FLUIDITY AND VISCOSITY OF WATER CALCULATED BY FORMULA[1]
FOR EVERY DEGREE BETWEEN 0° AND 100°C

Temperature, °C	Fluidity	Viscosity in cp	Temperature, °C	Fluidity	Viscosity in cp	Temperature, °C	Fluidity	Viscosity in cp
0	55.80	1.7921	33	132.93	0.7523	67	236.25	0.4233
1	57.76	1.7313	34	135.66	0.7371	68	239.57	0.4174
2	59.78	1.6728	35	138.40	0.7225	69	242.91	0.4117
3	61.76	1.6191	36	141.15	0.7085	70	246.26	0.4061
4	63.80	1.5674	37	143.95	0.6947	71	249.63	0.4006
5	65.84	1.5188	38	146.76	0.6814	72	253.02	0.3952
6	67.90	1.4728	39	149.60	0.6685	73	256.42	0.3900
7	70.01	1.4284	40	152.45	0.6560	74	259.82	0.3849
8	72.15	1.3860	41	155.30	0.6439	75	263.25	0.3799
9	74.28	1.3462	42	158.20	0.6321	76	266.67	0.3750
10	76.47	1.3077	43	161.11	0.6207	77	270.12	0.3702
11	78.66	1.2713	44	164.02	0.6097	78	273.57	0.3655
12	80.89	1.2363	45	167.00	0.5988	79	277.04	0.3610
13	83.14	1.2028	46	169.97	0.5883	80	280.53	0.3565
14	85.40	1.1709	47	172.95	0.5782	81	284.03	0.3521
15	87.69	1.1404	48	175.95	0.5683	82	287.53	0.3478
16	90.00	1.1111	49	178.95	0.5588	83	291.03	0.3436
17	92.35	1.0828	50	182.00	0.5494	84	294.54	0.3395
18	94.71	1.0559	51	185.05	0.5404	85	298.06	0.3355
19	97.10	1.0299	52	188.14	0.5315	86	301.63	0.3315
20	99.50	1.0050	53	191.23	0.5229	87	305.21	0.3276
20.20	100.00	1.0000	54	194.34	0.5146	88	308.78	0.3239
21	101.94	0.9810	55	197.45	0.5064	89	312.35	0.3202
22	104.40	0.9579	56	200.62	0.4985	90	315.92	0.3165
23	106.86	0.9358	57	203.78	0.4907	91	319.53	0.3130
24	109.38	0.9142	58	206.95	0.4832	92	323.13	0.3095
25	111.91	0.8937	59	210.13	0.4759	93	326.74	0.3060
26	114.45	0.8737	60	213.33	0.4688	94	330.38	0.3027
27	117.03	0.8545	61	216.54	0.4618	95	334.01	0.2994
28	119.62	0.8360	62	219.80	0.4550	96	337.65	0.2962
29	122.25	0.8180	63	223.07	0.4483	97	341.30	0.2930
30	124.89	0.8007	64	226.34	0.4418	98	344.96	0.2899
31	127.54	0.7840	65	229.64	0.4355	99	348.63	0.2868
32	130.22	0.7679	66	232.94	0.4293	100	352.30	0.2838

[1] $\phi = 2.1482\{(t - 8.435) + \sqrt{8078.4 + (t - 8.435)^2}\} - 120.$ *Cf.* p. 137.

TABLE IV.—FLUIDITY OF ALCOHOL-WATER MIXTURES[1]

Tempera-ture	Weight percentage of ethyl alcohol												
	0	10	20	30	39	40	45	50	60	70	80	90	100
	Volume percentage of ethyl alcohol at 25°C												
	0	12.36	24.09	35.23	44.92	45.83	50.94	55.93	65.56	74.80	83.59	92.01	100
0	55.8	30.2	18.8	14.4	13.8	14.0	14.4	15.2	17.4	21.0	27.1	36.6	56.4
5	65.8	38.8	24.6	18.9	17.8	17.9	18.2	19.0	21.6	25.6	32.0	43.3	61.6
10	76.5	45.9	31.6	24.7	22.8	22.8	23.0	23.9	26.5	30.6	36.9	47.6	68.2
15	87.7	55.8	38.2	30.7	28.4	28.3	28.5	29.1	31.8	36.1	43.3	55.5	75.1
20	99.5	65.0	45.8	36.9	34.7	34.4	34.7	34.8	37.4	42.2	49.8	62.1	83.3
25	111.9	75.6	55.1	45.9	42.5	42.5	41.9	41.7	44.6	49.1	57.2	70.2	91.2
30	124.9	86.2	64.4	53.4	50.0	49.4	49.5	49.6	51.9	56.6	65.3	78.2	99.7
35	138.4	99.4	75.1	63.3	58.6	58.3	57.7	58.0	60.1	65.4	73.8	87.2	109.4
40	152.4	110.2	86.2	73.1	67.9	67.5	66.9	66.7	69.1	74.4	83.1	96.6	119.9
45	167.0	123.2	98.5	84.1	77.9	77.6	76.5	77.3	78.7	84.1	92.5	106.5	130.8
50	182.0	136.3	110.2	95.2	89.0	88.3	87.1	86.6	88.7	94.2	103.3	117.9	142.5
55	197.4	150.9	122.9	107.6	100.7	100.2	98.4	98.0	100.3	106.0	115.3	130.8	155.2
60	213.3	164.3	135.8	119.9	113.0	112.0	110.3	109.5	110.8	116.8	126.7	142.1	168.9
65	229.6	180.5	150.1	133.0	125.3	124.7	122.6	122.3	124.1	130.6	140.7	156.0	181.5
70	246.3	194.5	164.5	146.4	138.0	137.5	135.2	135.1	137.2	143.9	153.9	169.9	198.6
75	263.2	210.2	178.8	160.3	151.5	150.8	148.9	148.7	150.8	157.1	166.6	183.0	212.5
80	280.5	232.7	198.1	176.4	167.1	166.5	164.1	163.5	165.7				

TABLE V.—SUCROSE SOLUTIONS, BINGHAM AND JACKSON

Tempera-ture	Percentage sucrose by weight				Tempera-ture	Percentage sucrose by weight			
	0	20	40	60		0	20	40	60
0	55.91	26.29	6.77	0.42	55	197.16	113.12	45.06	8.57
5	65.99	31.71	8.65	0.64	60	212.72	123.79	50.47	10.17
10	76.56	37.71	10.21	0.91	65	229.41	134.81	56.24	11.99
15	87.67	44.11	13.39	1.34	70	246.18	145.97	62.17	13.98
20	99.54	51.02	16.13	1.77	75	263.57	157.56	68.41	16.12
25	111.84	58.69	19.28	2.28	80	281.21	169.53	74.96	18.51
30	124.70	66.51	22.82	2.96	85	299.31	181.80	81.92	21.14
35	138.79	75.12	26.58	3.77	90	317.87	......	89.06	24.07
40	153.07	83.82	30.78	4.70	95	335.46	......	96.41	26.85
45	167.84	93.42	35.13	5.82	100	354.49	......	104.11	29.96
50	181.92	103.07	40.05	7.14					

[1] Values given are the weighted average of those of Stephan (1862), Pagliani and Batelli (1885), Traube (1886), Noack (1886) and Bingham and Thomas (1913).

TABLE VI.—RECIPROCALS

No.	0	1	2	3	4	5	6	7	8	9	Dif.
1.0	1.0000	9901	9804	9709	9615	9524	9434	9346	9259	9174	92
1.1	0.9091	9009	8929	8850	8772	8696	8621	8547	8475	8403	76
1.2	8333	8264	8197	8130	8065	8000	7937	7874	7813	7752	65
1.3	7692	7634	7576	7519	7463	7407	7353	7299	7246	7194	55
1.4	7143	7092	7042	6993	6944	6897	6849	6803	6757	6711	48
1.5	0.6667	6623	6579	6536	6494	6452	6410	6369	6329	6289	42
1.6	6250	6211	6173	6135	6098	6061	6024	5988	5952	5917	37
1.7	5882	5848	5814	5780	5747	5714	5682	5650	5618	5587	33
1.8	5556	5525	5495	5464	5435	5405	5376	5348	5319	5291	29
1.9	5263	5236	5208	5181	5155	5128	5102	5076	5051	5025	26
2.0	0.5000	4975	4950	4926	4902	4878	4854	4831	4808	4785	24
2.1	4762	4739	4717	4695	4673	4651	4630	4608	4587	4566	22
2.2	4545	4525	4505	4484	4464	4444	4425	4405	4386	4367	20
2.3	4348	4329	4310	4292	4274	4255	4237	4219	4202	4184	18
2.4	4167	4149	4132	4115	4098	4082	4065	4049	4032	4016	17
2.5	0.4000	3984	3968	3953	3937	3922	3906	3891	3876	3861	15
2.6	3846	3831	3817	3802	3788	3774	3759	3745	3731	3717	14
2.7	3704	3690	3676	3663	3650	3636	3623	3610	3597	3584	13
2.8	3571	3559	3546	3534	3521	3509	3496	3484	3472	3460	12
2.9	3448	3436	3425	3413	3401	3390	3378	3367	3356	3344	12
3.0	0.3333	3322	3311	3300	3289	3279	3268	3257	3247	3236	11
3.1	3226	3215	3205	3195	3185	3175	3165	3155	3145	3135	10
3.2	3125	3115	3106	3096	3086	3077	3067	3058	3049	3040	9
3.3	3030	3021	3012	3003	2994	2985	2976	2967	2959	2950	9
3.4	2941	2933	2924	2915	2907	2899	2890	2882	2874	2865	
3.5	0.2857	2849	2841	2833	2825	2817	2809	2801	2793	2786	8
3.6	2778	2770	2762	2755	2747	2740	2732	2725	2717	2710	7
3.7	2703	2695	2688	2681	2674	2667	2660	2653	2646	2639	
3.8	2632	2625	2618	2611	2604	2597	2591	2584	2577	2571	
3.9	2564	2558	2551	2545	2538	2532	2525	2519	2513	2506	
4.0	0.2500	2494	2488	2481	2475	2469	2463	2457	2451	2445	6
4.1	2439	2433	2427	2421	2415	2410	2404	2398	2392	2387	
4.2	2381	2375	2370	2364	2358	2353	2347	2342	2336	2331	
4.3	2326	2320	2315	2309	2304	2299	2294	2288	2283	2278	
4.4	2273	2268	2262	2257	2252	2247	2242	2237	2232	2227	5
4.5	0.2222	2217	2212	2208	2203	2198	2193	2188	2183	2179	
4.6	2174	2169	2165	2160	2155	2151	2146	2141	2137	2132	
4.7	2128	2123	2119	2114	2110	2105	2101	2096	2092	2088	
4.8	2083	2079	2075	2070	2066	2062	2058	2053	2049	2045	
4.9	2041	2037	2033	2028	2024	2020	2016	2012	2008	2004	
5.0	0.2000	1996	1992	1988	1984	1980	1976	1972	1969	1965	4
5.1	1961	1957	1953	1949	1946	1942	1938	1934	1931	1927	
5.2	1923	1919	1916	1912	1908	1905	1901	1898	1894	1890	
5.3	1887	1883	1880	1876	1873	1869	1866	1862	1859	1855	
5.4	1852	1848	1845	1842	1838	1835	1832	1828	1825	1821	
5.5	0.1818	1815	1812	1808	1805	1802	1799	1795	1792	1789	3
5.6	1786	1783	1779	1776	1773	1770	1767	1764	1761	1757	
5.7	1754	1751	1748	1745	1742	1739	1736	1733	1730	1727	
5.8	1724	1721	1718	1715	1712	1709	1706	1704	1701	1698	
5.9	1695	1692	1689	1686	1684	1681	1678	1675	1672	1669	

TABLE VI.—(*Continued*)

No.	0	1	2	3	4	5	6	7	8	9	Dif.
6.0	0.16667	16639	16611	16584	16556	16529	16502	16474	16447	16420	27
6.1	16393	16367	16340	16313	16287	16260	16234	16207	16181	16155	26
6.2	16129	16103	16077	16051	16026	16000	15974	15949	15924	15898	26
6.3	15873	15848	15823	15798	15773	15748	15723	15699	15674	15649	25
6.4	15625	15601	15576	15552	15528	15504	15480	15456	15432	15408	24
6.5	0.15385	15361	15337	15314	15291	15267	15244	15221	15198	15175	23
6.6	15152	15129	15106	15083	15060	15038	15015	14992	14970	14948	23
6.7	14925	14903	14881	14859	14837	14815	14793	14771	14749	14728	22
6.8	14706	14684	14663	14641	14620	14599	14577	14556	14535	14514	21
6.9	14493	14472	14451	14430	14409	14388	14368	14347	14327	14306	21
7.0	0.14286	14265	14245	14225	14205	14184	14164	14144	14124	14104	20
7.1	14085	14065	14045	14025	14006	13986	13966	13947	13928	13908	19
7.2	13889	13870	13850	13831	13812	13793	13774	13755	13736	13717	19
7.3	13699	13680	13661	13643	13624	13605	13587	13569	13550	13532	
7.4	13514	13495	13477	13459	13441	13423	13405	13387	13369	13351	18
7.5	0.13333	13316	13298	13280	13263	13245	13228	13210	13193	13175	
7.6	13158	13141	13123	13106	13089	13072	13055	13038	13021	13004	17
7.7	12987	12970	12953	12937	12920	12903	12887	12870	12853	12837	
7.8	12821	12804	12788	12771	12755	12739	12723	12706	12690	12674	16
7.9	12658	12642	12626	12610	12594	12579	12563	12547	12531	12516	
8.0	0.12500	12484	12469	12453	12438	12422	12407	12392	12376	12361	
8.1	12346	12330	12315	12300	12285	12270	12255	12240	12225	12210	15
8.2	12195	12180	12165	12151	12136	12121	12107	12092	12077	12063	
8.3	12048	12034	12019	12005	11990	11976	11962	11947	11933	11919	
8.4	11905	11891	11876	11862	11848	11834	11820	11806	11792	11779	14
8.5	0.11765	11751	11737	11723	11710	11696	11682	11669	11655	11641	
8.6	11628	11614	11601	11587	11574	11561	11547	11534	11521	11507	
8.7	11494	11481	11468	11455	11442	11429	11416	11403	11390	11377	13
8.8	11364	11351	11338	11325	11312	11299	11287	11274	11261	11249	
8.9	11236	11223	11211	11198	11186	11173	11161	11148	11136	11123	
9.0	0.11111	11099	11086	11074	11062	11050	11038	11025	11013	11001	
9.1	10989	10977	10965	10953	10941	10929	10917	10905	10893	10881	12
9.2	10870	10858	10846	10834	10823	10811	10799	10787	10776	10764	
9.3	10753	10741	10730	10718	10707	10695	10684	10672	10661	10650	
9.4	10638	10627	10616	10604	10593	10582	10571	10560	10549	10537	
9.5	0.10526	10515	10504	10493	10482	10471	10460	10449	10438	10428	11
9.6	10417	10406	10395	10384	10373	10363	10352	10341	10331	10320	
9.7	10309	10299	10288	10277	10267	10256	10246	10235	10225	10215	
9.8	10204	10194	10183	10173	10163	10152	10142	10132	10121	10111	
9.9	10101	10091	10081	10070	10060	10050	10040	10030	10020	10010	
10.0	0.10000	9990	9980	9970	9960	9950	9940	9930	9921	9911	10
10.1	09901	9891	9881	9872	9862	9852	9843	9833	9823	9814	
10.2	9804	9794	9785	9775	9766	9756	9747	9737	9728	9718	
10.3	9709	9699	9690	9681	9671	9662	9653	9643	9634	9625	
10.4	9615	9606	9597	9588	9579	9569	9560	9551	9542	9533	
10.5	0.09524	9515	9506	9497	9488	9479	9470	9461	9452	9443	9
10.6	9434	9425	9416	9407	9398	9390	9381	9372	9363	9355	
10.7	9346	9337	9328	9320	9311	9302	9294	9285	9276	9268	
10.8	9259	9251	9242	9234	9225	9217	9208	9200	9191	9183	
10.9	9174	9166	9158	9149	9141	9132	9124	9116	9107	9099	
11.0	0.09091	9083	9074	9066	9058	9050	9042	9033	9025	9017	8
11.1	9009	9001	8993	8985	8977	8969	8961	8953	8944	8937	8
11.2	8929	8921	8913	8905	8897	8889	8881	8873	8865	8857	8
11.3	8850	8842	8834	8826	8818	8811	8803	8795	8787	8780	8
11.4	8772	8764	8757	8749	8741	8734	8726	8718	8711	8703	8
11.5	0.08696	8689	8681	8673	8666	8658	8650	8643	8636	8628	7
11.6	8621	8613	8606	8598	8591	8584	8576	8569	8562	8554	7
11.7	8547	8540	8532	8525	8518	8511	8503	8496	8489	8482	7
11.8	8475	8467	8460	8453	8446	8439	8432	8425	8418	8410	7
11.9	8403	8396	8389	8382	8375	8368	8361	8354	8347	8340	7

FLUIDITY AND PLASTICITY

TABLE VI.—(*Continued*)

No.	0	1	2	3	4	5	6	7	8	9	Dif.
12.0	0.08333	8326	8320	8312	8306	8299	8292	8285	8288	8271	
12.1	8264	8258	8251	8244	8237	8230	8224 ·	8217	8210	8203	7
12.2	8197	8190	8183	8177	8170	8163	8157	8150	8143	8137	
12.3	8130	8124	8117	8110	8104	8097 ·	8091	8084	8078	8071	
12.4	8064	8058	8052	8045	8039	8032	8026	8019	8013	8006	
12.5	0.08000	7994	7987	7981	7974	7968	7962	7955	7949	7942	
12.6	7936	7930	7924	7918	7912	7905	7899	7893	7886	7880	
12.7	7874	7868	7862	7856	7849	7843	7837	7831	7825	7819	
12.8	7812	7806	7800	7794	7788	7782	7776	7770	7764	7758	
12.9	7752	7746	7740	7734	7728	7722	7716	7710	7704	7698	
13.0	0.07692	7686	7681	7675	7669	7663	7657	7651	7646	7640	6
13.1	7634	7628	7622 ·	7616	7610	7605	7599	7593	7587	7581	
13.2	7576	7570	7564	7559	7553	7547	7542	7536	7530	7524	
13.3	7519	7513	7508	7502	7496	7491	7485	7480	7474	7468	
13.4	7463	7457	7452	7446	7441	7435	7430	7424	7418	7413	
13.5	0.07407	7402	7396	7391	7386	7380	7375	7369	7364	7358	5
13.6	7353	7348	7342	7337	7332	7326	7321	7315	7310	7305	
13.7	7299	7294	7289	7283	7278	7273	7268	7262	7257	7252	
13.8	7246	7241	7236	7231	7226	7220	7215	7210	7205	7200	
13.9	7194	7189	7184	7179	7174	7169	7164	7158	7153	7148	
14.0	0.07143	7138	7133	7128	7123	7118	7113	7108	7102	7097	
14.1	7092	7087	7082	7077	7072	7067	7062	7057	7052	7047	
14.2	7042	7037	7032	7027	7022	7018	7013	7008	7003	6998	
14.3	6993	6988	6983	6978	6974	6969	6964	6959	6954	6949	
14.4	6944	6940	6935	6930	6925	6920	6916	6911	6906	6901	
14.5	0.06897	6892	6887	6882	6878	6873	6868	6863	6859	6854	5
14.6	6849	6845	6840	6835	6831	6826	6821	6817	6812	6807	
14.7	6803	6798	6793	6789	6784	6780	6775	6770	6766	6761	
14.8	6757	6752	6748	6743	6739	6734	6729	6725	6720	6716	
14.9	6711	6707	6702	6698	6693	6689	6684	6680	6676	6671	
15.0	0.06667	6662	6658	6653	6649	6645	6640	6636	6631	6627	
15.1	6623	6618	6614	6609	6605	6601	6596	6592	6588	6583	
15.2	6579	6575	6570	6566	6562	6557	6553	6549	6545	6540	
15.3	6536	6532	6527	6523	6519	6515	6510	6506	6502	6498	
15.4	6494	6489	6485	6481	6477	6472	6468	6464	6460	6456	
15.5	0.06452	6447	6443	6439	6435	6431	6427	6423	6419	6414	
15.6	6410	6406	6402	6398	6394	6390	6386	6382	6378	6373	
15.7	6369	6365	6361	6357	6353	6349	6345	6341	6337	6333	
15.8	6329	6325	6321	6317	6313	6309	6305	6301	6297	6293	4
15.9	6289	6285	6281	6277	6274	6270	6266	6262	6258	6254	
16.0	0.06250	6246	6242	6238	6234	6231	6227	6223	6219	6215	
16.1	6211	6207	6203	6200	6196	6192	6188	6184	6180	6177	
16.2	6173	6169	6165	6161	6158	6154	6150	6146	6143	6139	
16.3	6135	6131	6127	6124	6120	6116	6112	6109	6105	6101	
16.4	6097	6094	6090	6086	6083	6079	6075	6072	6068	6064	
16.5	0.06061	6057	6053	6050	6046	6042	6038	6035	6031	6028	
16.6	6024	6020	6017	6013	6010	6006	6002	5999	5995	5992	
16.7	5988	5984	5981	5977	5973	5970	5966	5963	5959	5956	
16.8	5952	5949	5945	5942	5938	5935	5931	5928	5924	5921	
16.9	5917	5914	5910	5907	5903	5900 ·	5896	5893	5889	5886	
17.0	0.05882	5879	5875	5872	5868	5865	5851	5858	5854	5851	
17.1	5847	5844	5841	5838	5834	5861	5828 ·	5824	5821	5817	
17.2	5814	5811	5807	5804	5800	5797	5794	5790	5787	5784	3
17.3	5780	5777	5774	5770	5767	5764	5760	5757	5754	5750	
17.4	5747	5744	5741	5737	5734	5731	5727	5724	5721	5718	
17.5	0.05714	5711	5708	5704	5701	5698	5695	5692	5688	5685	
17.6	5682	5679	5675	5672	5669	5666	5663	5659	5656	5653	
17.7	5650	5647	5643	5640	5637	5634	5631	5627	5624	5621	
17.8	5618	5615	5612	5609	5605	5602	5599	5596	5593	5590	
17.9	5587	5583	5580	5577	5574	5571	5568	5565	5562	5559	

TABLE VII.—LOGARITHMS

No.	0	1	2	3	4	5	6	7	8	9	Dif.
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	42
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	38
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	35
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	32
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	30
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	28
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	26
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	25
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	23
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	22
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	20
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	19
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	18
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	18
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	17
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	16
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	16
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	15
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	15
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	14
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	13
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	12
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	11
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	10
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8

TABLE VII.—(*Continued*)

No.	0	1	2	3	4	5	6	7	8	9	Dif.
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	
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